CHAPTER III

ELECTRICAL RELAXATION STUDIES OF HIGH ENERGY BALL-MILLED NASICON TYPE MATERIALS

3.1 Introduction

High energy ball-milling is a versatile method for the preparation of nanoceramics and this method has the control over the crystallite size by controlling the milling duration [1]. Ball-milling is used as a method for the synthesis of materials which are difficult to synthesize by conventional techniques like solid-state reaction. For the preparation of nanocrystalline material, stoichiometric mixture is ball-milled for long duration to reduce the size of the mixture to nanometer range. Milling reduces the crystallinity of the stoichiometric mixture and further heat treatments, at comparatively less temperature, are required to obtain the single phase nanocrystalline material. This process is called mechanically activated self-propagating high temperature synthesis.

Lithium titanium phosphate, LiTi$_2$(PO$_4$)$_3$ (LTP) is a NASICON type, Li$^+$ ion conducting polycrystalline material in rhombohedral symmetry with R$ar{3}$c space group. The room temperature conductivity of LTP is low for practical applications [2, 3] and several methods have been tried to increase its conductivity. One of the methods is, the addition of lithium salts to enhance the density of the material [3, 4]. Another technique is the partial substitution of Ti$^{4+}$ by trivalent cations; out of which Li$_{1.3}$Al$_{0.3}$Ti$_{1.7}$(PO$_4$)$_3$ [LATP] shows the highest ionic conductivity of $10^{-3}$Scm$^{-1}$ at room temperature [5]. A number of attempts have been reported in literature to increase the conductivity of LATP further; which includes various synthesis techniques, spark plasma sintering [6], partial substitution of phosphorous in LATP by pentavalent cations like V$^{5+}$, Nb$^{5+}$ and Ta$^{5+}$. Gromov et al., reported an increase in the ionic conductivity by vanadium substitution, which was in contrary to the results reported by Best et al., [7]. Different chemical synthesis methods are also tried to increase the conductivity.

High energy ball-milling is a promising method for sample preparation [8, 9]; a few reviews are available about the role of ball-milling in enhancing the electrical conductivity properties of NASICON type polycrystalline materials. For the present study, low conducting LTP and high conducting vanadium substituted LATP series
have been considered for the high energy ball-milling technique to explore the possibilities of raising the electrical conductivity further in these systems. The materials explored in this study are:

(i) LiTi$_2$(PO$_4$)$_3$
(ii) Li$_{1.3}$Al$_{0.3}$Ti$_{1.7}$(PO$_4$)$_{2.9}$(VO$_4$)$_{0.1}$
(iii) Li$_{1.0}$Al$_{0.4}$Ti$_{1.7}$(PO$_4$)$_{2.88}$(VO$_4$)$_{0.12}$
(iv) Li$_{1.6}$Al$_{0.2}$Ti$_{1.7}$(PO$_4$)$_{2.94}$(VO$_4$)$_{0.06}$

The present study compares the electrical properties of microcrystalline LiTi$_2$(PO$_4$)$_3$ with that of nanocrystalline material. The conventional solid-state reaction produces crystallites of micrometer size, while solid-state reaction of 40h ball-milled stoichiometric mixture produces nanometer sized crystallites. In addition to this, vanadium substituted LATP materials are ball-milled in different durations. This reduces the average crystallite size to different ranges depending on the milling duration. The present work reports the structural characteristics and the electrical conductivity studies of the ball-milled and the corresponding microcrystalline materials. XRD, FT-IR and SEM are used for the structural characterisations. Ac electrical studies are carried out by exploiting the impedance/dielectric spectroscopy.

### 3.2 Experimental Details

Microcrystalline material is prepared by the conventional solid-state reaction of the stoichiometric mixture of Li$_2$CO$_3$ (Himedia, 99.0%), NH$_4$H$_2$PO$_4$ (Himedia, 99.0%), TiO$_2$ (LR grade, 98.0%), Al$_2$O$_3$ (Himedia, 99.0%) and V$_2$O$_5$ (Himedia, 99.0%). Overall reaction for the formation of LiTi$_2$(PO$_4$)$_3$ and Li$_{1.3}$Ti$_{1.7}$Al$_{0.3}$(PO$_4$)$_{2.9}$(VO$_4$)$_{0.1}$ [LATPV$_{0.1}$] are given [10]:

\[0.5\text{Li}_2\text{CO}_3 + 2\text{TiO}_2 + 3\text{NH}_4\text{H}_2\text{PO}_4 \xrightarrow{\Delta} \text{LiTi}_2(\text{PO}_4)\text{3} + 3\text{NH}_3 + 0.5\text{CO}_2 + 4.5\text{H}_2\text{O}\] (3.1)

\[0.65\text{Li}_2\text{CO}_3 + 1.7\text{TiO}_2 + 0.15\text{Al}_2\text{O}_3 + 2.9\text{NH}_4\text{H}_2\text{PO}_4 + 0.05\text{V}_2\text{O}_5 \xrightarrow{\Delta} \text{Li}_{1.3}\text{Ti}_{1.7}\text{Al}_{0.3}(\text{PO}_4)\text{2.9}(\text{VO}_4)\text{0.1} + 0.65\text{CO}_2 + 2.9\text{NH}_3 + 4.35\text{H}_2\text{O}\] (3.2)

Various steps involved in the synthesis of microcrystalline materials are:

(i) Stoichiometric amounts of starting reagents were ground in an agate mortar for 45 minutes.
(ii) The mixture is placed in a silica crucible and slowly heated in an electric furnace up to 523K. Further, the temperature is increased to 623K and held at this temperature for 6h in order to ensure the total decomposition of the initial reagents.

(iii) After cooling the mixture to room temperature, it is again ground for 45min in an agate mortar and pellets of 10mm diameter and 1-1.5mm thickness was formed. Then pellets were heat treated at 923K for 6h. Heating procedure remains the same for both LTP and LATPV series till this stage.

(iv) Further, LTP pellets were calcined at 1073K for 36h followed by sintering at 1223K for 2h. In the meanwhile, the pellets of LATPV series were calcined at 1073K for 48h followed by sintering at 1323K for 4h.

Smaller crystallite sized materials were prepared through conventional solid-state reaction of the ball-milled stoichiometric mixture. The mixture is heated at 623K before ball-milling to remove the gases and water content. This minimizes sticking property of the mixture to the vial and balls. The tungsten carbide vial and balls were used for high energy milling; the typical ball to powder mass ratio is kept at 5:1 throughout the milling. The rotation speed is kept at 300rpm, each cycle comprised of 2h run followed by 30minutes pause, and these cycles were repeated. Milling is carried out in an ethanol medium in case of LATPV series, which acts as a surfactant to decrease the agglomeration and helps to reduce the heat produced while milling. The powder obtained after milling is made into pellets and further heat treatments were applied from 923K to 1223K for LTP, and 923K to 1323K for LATPV series with the same duration as the microcrystalline sample. In this study, applied sintering temperature is less than the conventional ceramic route. Even though, the sintering temperature is low, long hours of sintering are performed to obtain the required density for samples [11]. Low temperature sintering is applied to maintain the nanocrystalline nature of the samples.

The X-ray powder diffraction patterns were collected using Philips X’pert pro-diffractometer with Bragg-Brentano geometry with 0-0 configuration. The monochromatic Cu Kα1 radiation of wavelength, λ = 1.5406Å is used. The pattern is recorded in the 2θ range 5º-75º with step size of 0.02º and the step scan of 0.50
seconds. Ac electrical measurements were carried out in the temperature range from 309K to 388K by sandwiching the pellet between two silver electrodes. The parallel conductance (G) and capacitance (C) of the material were acquired in the frequency range 100Hz-1MHz using HIOKI 3532-50LCR Hi-Tester at different temperatures.

3.3 Results and Discussion

3.3.1 Structural Characterizations

3.3.1.1 X-ray Powder Diffraction Analysis

Figs. 3.1(a)-(b) show XRD patterns of the microcrystalline and 40h ball-milled LiTi$_2$(PO$_4$)$_3$ pellets after sintering at 1073K. The peaks in the XRD pattern correspond to the single phase of LiTi$_2$(PO$_4$)$_3$ material while, XRD pattern of the materials sintered at high temperatures contain few minor peaks of TiP$_2$O$_7$ phase in the low 2$\theta$ range up to 29° due to Li loss at high temperatures [12, 13]. But the patterns with the minority phase are not given in Figs. 3.1(a)-(b). The Fig. 3.1(c) shows XRD patterns of Li$_{1.3}$Ti$_{1.7}$Al$_{0.3}$(PO$_4$)$_{2.9}$(VO$_4$)$_{0.1}$ materials.

![Figure 3.1](image-url)

**Figure 3.1:** Shows X-ray powder diffraction patterns of (a) microcrystalline LiTi$_2$(PO$_4$)$_3$ (b) nanocrystalline LiTi$_2$(PO$_4$)$_3$ (c) Li$_{1.3}$Ti$_{1.7}$Al$_{0.3}$(PO$_4$)$_{2.9}$(VO$_4$)$_{0.1}$ microcrystalline, 22h and 55h ball-milled material and (d) Full width at half maximum of maximum intensity peak of the microcrystalline, 22h and 55h ball-milled Li$_{1.3}$Ti$_{1.7}$Al$_{0.3}$(PO$_4$)$_{2.9}$(VO$_4$)$_{0.1}$. 
The lattice parameters of LTP are given in Table 3.1. These parameters are calculated using UNITCELL software [14] for sintered pellets, which shows that the ball-milling decreases the lattice parameters [15] and the unit cell volume. While, the lattice parameters of Li_{1.3}Ti_{1.7}Al_{0.3}(PO_{4})_{2.9}(VO_{4})_{0.1} increases [16] with increased milling duration as given in Table 3.2. In almost all cases, the line broadening in XRD occurs due to the simultaneous size and strain effects [17], because the high energy ball-milling introduces considerable strain in the material. The effect of strain is observed in broadening the XRD peak and shift in the peak positions towards the higher 2θ values. Williamson and Hall [18] developed a model to separate the size and strain effects in the broadening of X-ray diffraction peaks and is given by:

\[ B\cos\theta = \frac{K\lambda}{D} + 4\varepsilon\sin\theta \]  

(3.3)

where, \(B\) is the full width at half maximum (FWHM) of XRD peaks, \(K\) is the Scherrer constant, \(D\) is the crystallite size, \(\lambda\) is the wavelength of the X-ray, \(\varepsilon\) is the micro-strain in the lattice and \(\theta\) is the Bragg angle. For Gaussian X-ray profiles, \(B\) can be calculated as:

\[ B^2 = B_m^2 - B_s^2 \]  

(3.4)

where, \(B_m\) is the FWHM of the material and \(B_s\) is the FWHM of a standard sample; silicon is taken as the standard for the calculation of instrumental parameters. Linear extrapolation of the plot of \(B\cos\theta \text{ vs } 4\sin\theta\) gives the average crystallite size from the intercept, \(\frac{K\lambda}{D}\) and the slope gives the micro-strain. While, for microcrystalline materials, the crystallite size is calculated using Eq. (3.3), where the strain contribution is negligible. The micro-strain and crystallite sizes of LiTi_{2}(PO_{4})_{3} and Li_{1.3}Ti_{1.7}Al_{0.3}(PO_{4})_{2.9}(VO_{4})_{0.1} are calculated and listed in Table 3.1 & 3.2 respectively.

**Table 3.1**: Average crystallite size, micro-strain and the unit cell parameters of the microcrystalline and the nanocrystalline LiTi_{2}(PO_{4})_{3} pellets after sintering.

<table>
<thead>
<tr>
<th>LiTi_{2}(PO_{4})_{3}</th>
<th>Average crystallite size</th>
<th>Micro-strain</th>
<th>Unitcell parameters*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>a [Å]</td>
</tr>
<tr>
<td>Microcrystalline</td>
<td>0.2µm</td>
<td>0.05%</td>
<td>8.514(9)</td>
</tr>
<tr>
<td>Nano crystalline</td>
<td>70nm</td>
<td>0.36%</td>
<td>8.495(9)</td>
</tr>
</tbody>
</table>

*calculated by UNITCELL program assuming the hexagonal symmetry.
Ball-milling induces strain in lattice and decreases the average crystallite size to 70nm for 40h ball-milled LiTi_2(PO_4)_3 material. Milling reduces the average crystallite size to nanometer range. But there are evidences that long hours of ball-milling lead to the formation of an amorphous state [19]. Hence, sintering at high temperature after ball-milling resulted in the formation of nanocrystallites instead of microcrystalline material. XRD pattern gradually broadened and the particle size decreased with milling time, which is clear from FWHM of the highest intensity peaks of ball-milled Li_{1.3}Ti_{1.7}Al_{0.3}(PO_4)_{2.9}(VO_4)_{0.1} given in Fig. 3.1(d). The nanocrystalline nature of the ball-milled materials is evident in the broadened peak and there is decrease in the intensity of XRD peak compared to the microcrystalline material. Calculated and measured density of calcined Li_{1.3}Ti_{1.7}Al_{0.3}(PO_4)_{2.9}(VO_4)_{0.1} samples are given in Table 3.2. Other members of the LATPV series validate the same tendency of decrease in crystallite size and increase in lattice parameters with increasing ball-milling duration.

### Table 3.2: Average crystallite size, density, micro-strain and unit cell parameters of microcrystalline, 22h and 55h ball-milled Li_{1.3}Ti_{1.7}Al_{0.3}(PO_4)_{2.9}(VO_4)_{0.1} pellets calcined at 1073K.

<table>
<thead>
<tr>
<th>LATPV_{0.1}</th>
<th>Average crystallite size</th>
<th>Density [gmcm^{-3}]</th>
<th>Micro-strain (%)</th>
<th>Unit cell parameters*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Theoretical</td>
<td>Measured</td>
<td></td>
</tr>
<tr>
<td>Microcrystalline</td>
<td>1.60μm</td>
<td>2.957</td>
<td>2.646</td>
<td>0.02</td>
</tr>
<tr>
<td>22h ball-milled</td>
<td>86.62nm</td>
<td>2.954</td>
<td>2.644</td>
<td>0.29</td>
</tr>
<tr>
<td>55h ball-milled</td>
<td>60.86nm</td>
<td>2.945</td>
<td>2.677</td>
<td>0.62</td>
</tr>
</tbody>
</table>

*Unit cell parameters are calculated from XRD data using UNITCELL software assuming the hexagonal symmetry.

#### 3.3.1.2 FT-IR Analysis

The FT-IR absorption bands of ball-milled materials of LATPV series in the range 4000cm^{-1}-400cm^{-1} are shown in Fig. 3.2. The entire region down to 400cm^{-1} is dominated by vibrations of PO_4 tetrahedra group. Bands observed in the region 580-450cm^{-1} for all samples are attributed to the harmonics of P–O–P bending vibrations [20]. Stretching vibrations of P–O–P bond are identified in the region 700-758cm^{-1}.
The bands in the region ~560 cm\(^{-1}\) are attributed to the asymmetric bending vibrational modes of O–P–O units [20-23]. Vibration of PO\(_3^2\)-ionic group can be seen at 931-882 cm\(^{-1}\) [23]. The bands in the region 1082-940 cm\(^{-1}\) indicate the presence of PO\(_4^3\)-ionic group [20, 24, 25]. Further, FT-IR spectra show weak peak of carbonates in the region 1400-1600 cm\(^{-1}\). The asymmetric stretching vibration of VO\(_4\) tetrahedra is observed at 810-850 cm\(^{-1}\) as broad band. In addition, oxygen atom in the VO\(_4\) tetrahedra can form bond with Al atom which can lead to some asymmetry. Hence, the broad band in the region 810-850 cm\(^{-1}\) is assigned to be the asymmetrical stretching mode in the distorted VO\(_4\) unit [26]. The stretching modes of VO\(_4\) in the IR spectra confirm the substitution of vanadium for phosphorus in PO\(_4\) tetrahedra.

![FT-IR spectra of 22h and 55h ball-milled Li\(_{1.3}\)Ti\(_{1.7}\)Al\(_{0.3}\)(PO\(_4\))\(_{2.9}\)(VO\(_4\))\(_{0.1}\) and Li\(_{1.0}\)Al\(_{0.4}\)Ti\(_{1.7}\)(PO\(_4\))\(_{2.88}\)(VO\(_4\))\(_{0.12}\) materials.](image)

**Figure 3.2:** Shows the FT-IR spectra of 22h and 55h ball-milled Li\(_{1.3}\)Ti\(_{1.7}\)Al\(_{0.3}\)(PO\(_4\))\(_{2.9}\)(VO\(_4\))\(_{0.1}\) and Li\(_{1.0}\)Al\(_{0.4}\)Ti\(_{1.7}\)(PO\(_4\))\(_{2.88}\)(VO\(_4\))\(_{0.12}\) materials.

### 3.3.1.3 SEM-EDS Analysis

SEM images in Figs. 3.3(a)-(b) show the surface morphology of the microcrystalline (MCM) and 55h ball-milled nanocrystalline LTP pellets after calcination. The small crystallites in nanocrystalline LTP are agglomerated and its size distribution is not uniform due to dry milling [27]. EDS is used for the quantitative chemical analysis of the materials, but EDS detector cannot detect elements with atomic number less than four, hence Li metal cannot be detected by this technique. The Fig. 3.3(c) shows EDS spectrum of 55h ball-milled LTP material and
Inset table give atomic and weight percentage of elements present in the material except Li.

**Figure 3.3:** Schematic of SEM images of (a) microcrystalline (b) 55h ball-milled LiTi$_2$(PO$_4$)$_3$ pellets after sintering at 1073K (c) EDS spectrum of 55h ball-milled LiTi$_2$(PO$_4$)$_3$ and inset table provides atomic and weight percentage of elements present in the material.

Surface morphology of LATPV$_{0.1}$ material also shows agglomeration of crystallites in the ball-milled samples, and the particle size decreases with milling duration as shown in Figs. 3.4(a)-(c). X-ray mapping is an imaging technique performed using the X-ray. This analytical technique provides a high magnification image related to the distribution and relative abundance of elements within a given specimen. This technique is useful for: (i) identifying the location of individual elements and (ii) mapping the spatial distribution of specific elements and phases in the material surface. Figs. 3.4(d(ii)-(vi)) show X-ray dot mapping of the SEM image of the 55h ball-milled Li$_{1.3}$Ti$_{1.7}$Al$_{0.3}$(PO$_4$)$_2.9$(VO$_4$)$_{0.1}$ material shown in d(i). Elemental analysis shows peaks corresponding to Ti, Al, P and O elements present in the material. The inset table in Fig. 3.4(e) give weight and atomic percentage of elements present in 55h ball-milled Li$_{1.3}$Ti$_{1.7}$Al$_{0.3}$(PO$_4$)$_2.9$(VO$_4$)$_{0.1}$ material. The percentages of elements that are detected by instrument and calculated from molecular formula fall within the error.

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Atom %</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>26.04</td>
<td>47.08</td>
</tr>
<tr>
<td>P</td>
<td>25.00</td>
<td>23.35</td>
</tr>
<tr>
<td>Ti</td>
<td>48.96</td>
<td>29.57</td>
</tr>
</tbody>
</table>
3.3.2 Electrical Characterization

3.3.2.1 Impedance Spectroscopy Analysis

The real part, $Z'(\omega)$ and the imaginary part, $Z''(\omega)$ of the complex impedance $Z^*(\omega)=Z'(\omega)-iZ''(\omega)$ are calculated from the measured G and C values as:

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight [%]</th>
<th>Atom [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>O K</td>
<td>47.41</td>
<td>68.61</td>
</tr>
<tr>
<td>Al K</td>
<td>3.22</td>
<td>2.76</td>
</tr>
<tr>
<td>P K</td>
<td>18.24</td>
<td>13.64</td>
</tr>
<tr>
<td>Ti K</td>
<td>29.44</td>
<td>14.23</td>
</tr>
<tr>
<td>V K</td>
<td>1.68</td>
<td>0.76</td>
</tr>
</tbody>
</table>
where, $\omega=2\pi f$, $f$ being the frequency in Hertz.

The elements of an equivalent circuit model represent various (macroscopic) processes involved in the transport of mass and charge. Using NLLS techniques, all the parameters in the equivalent circuit are adjusted simultaneously, thus obtaining the optimum fit to the measured dispersion data. A more general NLLS-fit program based on the Marquardt algorithm has been used. The impedance parameters are obtained by fitting the data to an equivalent circuit using NLLS fitting procedure due to Boukamp [28-30].

Figure 3.5: The complex impedance spectra of (a) microcrystalline $\text{LiTi}_2(\text{PO}_4)_3$ at 368K and (b) nanocrystalline $\text{LiTi}_2(\text{PO}_4)_3$ at 348K. Inset of Fig. 3.5 (a) and (b) shows grain part of the corresponding equivalent circuit and the continuous line is the simulation result.

Figs. 3.5(a) and (b) show the complex impedance plane plot of microcrystalline $\text{LiTi}_2(\text{PO}_4)_3$ material at 368K and nanocrystalline $\text{LiTi}_2(\text{PO}_4)_3$ material at 348K. For both of these materials equivalent circuit model is the same throughout the temperature range from 309K to 388K. Equivalent circuit model consists of two depressed semi-circles, where the high frequency semi-circle is displaced from the origin. Since, the high frequency semi-circle is impeded by the low frequency one and effectively only one semi-circle can be visible in the complex impedance plane plot. The ratio of grain capacitance to the grain-boundary
capacitance should be less than $10^{-3}$ for the appearance of two separate semi-circles in the complex impedance plane plot [31]. Inset of Figs. 3.5(a)-(b) show the high frequency part in the complex impedance plane plot, where continuous line is the simulation result. Simulation clearly shows the grain semi-circle, which is not seen explicitly in the complex impedance representation of the equivalent circuit.

The impedance plane plots are depressed due to the distribution of relaxation times; a non-ideal capacitor or the CPE, $Q$, is used to explain the depressed semi-circle [32]. Equivalent circuit of the impedance plane plots obtained using the Boukamp equivalent circuit analysis is found to be $R_c(R_g Q_g)(R_{gb} Q_{gb})$. Resistance of the electrolyte-electrode contact is $R_c$, which is characterized by the shift of the impedance arc from the origin. Constant phase elements, $Q_g$ and $Q_{gb}$ represent the grain and grain-boundary property of the sample. Grain resistance, $R_g$ and the grain-boundary resistance, $R_{gb}$ of the sample are obtained by right and left intercepts of the semi-circles with the real axis. $R_g$ and $R_{gb}$ are used to calculate the corresponding grain conductivity, $\sigma_{dcg}$ and grain-boundary conductivity, $\sigma_{dcbg}$. The obtained equivalent circuit is the same for both the LiTi$_2$(PO$_4$)$_3$ samples, but with the different magnitudes of circuit parameters.

For both the samples, $R_c$ variation is not consistent with temperature, $R_g$ and $R_{gb}$ of both the samples decrease with increase in temperature, $Q_{gb}$ values increases with temperature, while, $Q_g$ decreases. The grain conductivity at 309K ($\sigma_{dcg309K}=1.82\times10^{-6} \text{S cm}^{-1}$) of the microcrystalline material is consistent with the reported room temperature value of $10^{-7} \text{S cm}^{-1}$ [11]. At 388K, grain conductivity ($\sigma_{dcg388K}=8.57\times10^{-4} \text{S cm}^{-1}$) of nanocrystalline material shows an order of magnitude jump [33] compared to the microcrystalline material ($\sigma_{dcg388K}=7.74\times10^{-5} \text{S cm}^{-1}$). This significant increase in the grain conduction resulted from the reduced crystallite size. High energy ball-milling introduces grain-boundaries in the material and its volume fraction is more in nanocrystalline material. The diffusion through grain-boundaries is much faster than the grain diffusion; hence large volume fractions of grain-boundaries play a dominant role in ion conduction [34].

Figs. 3.6(a)-(b) show Arrhenius plot of grain and grain-boundary conductivity of the microcrystalline and nanocrystalline LiTi$_2$(PO$_4$)$_3$ material. The Arrhenius equation is given by:
\[ \sigma_{\text{dc}} T = \sigma_0 \exp \left( -\frac{E_\sigma}{k_B T} \right) \]  

(3.7)

where, \( \sigma_{\text{dc}} \) is the dc conductivity, \( \sigma_0 \) is the pre-exponential factor, \( T \) is the temperature in Kelvin, \( E_\sigma \) is the activation energy for dc conduction and \( k_B \) is the Boltzmann’s constant.

![Figure 3.6: Arrhenius plot of (a) grain and (b) grain-boundary conductivity of microcrystalline and nanocrystalline LiTi_2(PO_4)_3 material. Solid line represents best fit to the Eq. (3.7).](image)

From the slope of the Arrhenius plots, grain and grain-boundary activation energies \( E_{\text{ag}} \) and \( E_{\text{agb}} \) are calculated and are shown in Table 3.3. Increase in the grain conductivity of the nanocrystalline material is due to the feasible conduction through the grain-boundaries as its activation energy for grain-boundary conduction is less compared to the grain conduction [33]. Even though the ball-milling decreases the crystallite size, its distribution is not uniform due to dry milling. The non-uniform size distribution and agglomeration are the causes of higher activation energy in nanocrystalline LiTi_2(PO_4)_3 material, in spite of its higher conductivity [33]. These agglomerated crystallites are seen clearly in SEM images. Table 3.4 provides the charge carrier concentration, \( n_c \), (calculated using Eq. 2.16) of microcrystalline and nanocrystalline LiTi_2(PO_4)_3 material, which authenticate that the ball-milling does not increase the carrier concentration.
Table 3.3: Activation energies and dc conductivity values of microcrystalline and nanocrystalline LiTi$_2$(PO$_4$)$_3$ materials.

<table>
<thead>
<tr>
<th>LiTi$_2$(PO$_4$)$_3$</th>
<th>Activation energy for conduction through [eV]</th>
<th>Grain conductivity [Scm$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Grain $E_g$</td>
<td>Grain-boundary $E_{gb}$</td>
</tr>
<tr>
<td>Microcrystalline</td>
<td>(0.54±0.02)</td>
<td>(0.34±0.02)</td>
</tr>
<tr>
<td>Nanocrystalline</td>
<td>(0.76±0.03)</td>
<td>(0.42±0.02)</td>
</tr>
</tbody>
</table>

Table 3.4: Carrier concentration of microcrystalline and nanocrystalline LiTi$_2$(PO$_4$)$_3$ materials over the temperature range 302K to 396K.

<table>
<thead>
<tr>
<th>Temperature [K]</th>
<th>Carrier concentration, $n_c$ [cm$^{-3}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Microcrystalline 40h Ball-milled</td>
</tr>
<tr>
<td>302</td>
<td>2.40x10$^{20}$</td>
</tr>
<tr>
<td>310</td>
<td>2.01x10$^{20}$</td>
</tr>
<tr>
<td>317</td>
<td>2.36x10$^{20}$</td>
</tr>
<tr>
<td>328</td>
<td>2.16x10$^{20}$</td>
</tr>
<tr>
<td>338</td>
<td>2.12x10$^{20}$</td>
</tr>
<tr>
<td>348</td>
<td>2.13x10$^{20}$</td>
</tr>
<tr>
<td>358</td>
<td>1.98x10$^{20}$</td>
</tr>
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<td>368</td>
<td>1.95x10$^{20}$</td>
</tr>
<tr>
<td>378</td>
<td>2.17x10$^{20}$</td>
</tr>
<tr>
<td>388</td>
<td>1.84x10$^{20}$</td>
</tr>
<tr>
<td>396</td>
<td>1.76x10$^{20}$</td>
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</tbody>
</table>

The impedance plane plots of Li$_{1.3}$Ti$_{1.7}$Al$_{0.3}$(PO$_4$)$_{2.9}$(VO$_4$)$_{0.1}$ material shows obvious indication of blocking effect at the grain-boundaries and at the electrode-sample interface. Figs. 3.7(a)-(c) show impedance plots of microcrystalline and ball-milled materials. Equivalent circuit consists of series combination of a semi-circle associated to grain-boundary contribution and spike characterizing the electrode disparity at the low frequency part. The equivalent circuit representation is $(R_{gb}Q_{gb}C_{gb})$ up to 85°C and at higher temperatures it becomes $(R_{gb}Q_{gb})(Q_cC_e)$ for the microcrystalline material. In the case of 22h ball-milled material, the equivalent
circuit representation is \( (R_{gb}Q_{gb}C_{gb})(Q_{e}C_{e}) \) in the whole temperature range. Impedance plane plots of 55h ball-milled material show overlapped semicircles; in which the high frequency arc is attributed to the grain contribution.

![Figure 3.7: Complex impedance spectra of (a) microcrystalline (b) 22h and (c) 55h ball-milled Li\(_{1.3}\)Ti\(_{1.7}\)Al\(_{0.3}\)(PO\(_4\))\(_{2.9}\)(VO\(_4\))\(_{0.1}\) material at 95°C. In Fig. 3.7(c) inset shows simulation to the grain semi-circle.](image)

Inset of Fig. 3.7 (c) shows the high frequency part in the complex impedance plane plot where continuous line is the simulation result. Simulation clearly shows the grain semi-circle, which is not seen explicitly in the complex impedance plane representation. The high frequency studies are requisite to obtain the grain contribution of microcrystalline and 22h ball-milled material. Mechanical milling changes the capacitive contribution in such a way that in 55h ball-milled material, grain contribution is substantial within the frequency window [33]. Mechanical milling decreases the difference between the grain and grain-boundary capacitance values; which indicates relatively good connectivity between the grains. Using the NLLS technique, all the parameters in the equivalent circuit are adjusted simultaneously; thus obtaining the optimum fit to the measured dispersion data. The NLLS fit procedure due to Boukamp [28-32] is used to separate grain and grain-boundary contributions to the electrical response.

Table 3.5 provides the dc conductivity values and the activation energies of microcrystalline and ball-milled Li\(_{1.3}\)Ti\(_{1.7}\)Al\(_{0.3}\)(PO\(_4\))\(_{2.9}\)(VO\(_4\))\(_{0.1}\) materials. Grain-boundary conductivity of 55h ball-milled material at 65°C illustrates an order of magnitude increase in comparison to the microcrystalline counterpart as shown in Fig. 3.8(a). High frequency investigation is needed to explore the grain characteristics of
the microcrystalline and 22h ball-milled material. Micro-strain induced by the milling creates defects like grain-boundaries and its volume fraction is much more in ball-milled samples. Ions can diffuse faster through grain-boundaries and it is reflected in the observed jump in the conductivity in the 55h ball-milled material [33]. The ease of ion diffusion through grain-boundary is reflected in the values of activation energy as given in Table 3.5. With the milling duration activation energy decreases since the ion diffusion become easier as the volume fraction of the grain-boundaries increases.

Table 3.5: Conductivity and activation energy of the grain-boundary and grain conduction in microcrystalline and ball-milled Li$_{1.3}$Ti$_{1.7}$Al$_{0.3}$(PO$_{4}$)$_{2.9}$(VO$_{4}$)$_{0.1}$ materials.

<table>
<thead>
<tr>
<th>LATPV$_{0.1}$</th>
<th>Grain-boundary</th>
<th>Grain</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Conductivity at 65°C $\sigma_{dcgb}$[Scm$^{-1}$]</td>
<td>Activation energy $E_{dcgb}$[eV]</td>
</tr>
<tr>
<td>Microcrystalline</td>
<td>3.75x10$^{-8}$</td>
<td>(0.73±0.090)</td>
</tr>
<tr>
<td>22h ball-Milled</td>
<td>1.28x10$^{-7}$</td>
<td>(0.65±0.007)</td>
</tr>
<tr>
<td>55h ball-milled</td>
<td>3.13x10$^{-7}$</td>
<td>(0.26±0.040)</td>
</tr>
</tbody>
</table>

Figure 3.8: Arrhenius plots of (a) grain-boundary conductivity of microcrystalline, grain and grain-boundary conductivity of 55h ball-milled Li$_{1.3}$Ti$_{1.7}$Al$_{0.3}$(PO$_{4}$)$_{2.9}$(VO$_{4}$)$_{0.1}$ material (b) grain conductivity of microcrystalline, 44h and 55h ball-milled Li$_{1}$Ti$_{1.7}$Al$_{0.4}$(PO$_{4}$)$_{2.88}$(VO$_{4}$)$_{0.12}$ material. The solid line represents best fit to the Arrhenius Eq. (3.7).

Fig. 3.8(b) shows grain conductivity values of different hours ball-milled Li$_{1}$Ti$_{1.7}$Al$_{0.4}$(PO$_{4}$)$_{2.88}$(VO$_{4}$)$_{0.12}$ material. Conductivity values of 44h ball-milled material are even lesser than the microcrystalline material. The 55h ball-milled
material shows a little increase in conductivity (less than one order) compared to the microcrystalline material, but this trend is observable only in the high temperature region. The corresponding conductivity values and the activation energies are listed in Table 3.6. In \( \text{Li}_{1.6}\text{Al}_{0.2}\text{Ti}_{1.7}(\text{PO}_4)_{2.94}(\text{VO}_4)_{0.06} \), 55h ball-milled material shows both grain and grain-boundary contributions. But the microcrystalline and 22h ball-milled materials show only grain-boundary contributions in the investigated frequency range. In this material the grain-boundary conductivity and the dc activation energy did not show uniform trend with the ball-milling duration.

**Table 3.6:** Conductivity and activation energy of the grain-boundary and grain in microcrystalline and ball-milled \( \text{Li}_{1.3}\text{Ti}_{1.7}\text{Al}_{0.3} \) \( \text{PO}_4 \) \( \times \text{VO}_4 \) \( \times \text{PO}_4 \) materials.

<table>
<thead>
<tr>
<th>LATPV(_{0.12})</th>
<th>Conductivity at 140 C ( [\text{Scm}^{-1}] )</th>
<th>Activation energy ( [\text{eV}] )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Grain-boundary ( \sigma_{\text{dcgb}} )</td>
<td>Grain ( \sigma_{\text{dcg}} )</td>
</tr>
<tr>
<td>Microcrystalline</td>
<td>( 3.17 \times 10^{-5} )</td>
<td>---</td>
</tr>
<tr>
<td>44h ball-milled</td>
<td>( 1.59 \times 10^{-5} )</td>
<td>---</td>
</tr>
<tr>
<td>55h ball-milled</td>
<td>( 4.18 \times 10^{-5} )</td>
<td>( 1.43 \times 10^{-6} )</td>
</tr>
</tbody>
</table>

### 3.3.2.2 Permittivity Representation

The real part, \( \varepsilon'(\omega) \) and imaginary part, \( \varepsilon''(\omega) \) of the complex dielectric constant \( \varepsilon^*(\omega) \) are calculated from equations as:

\[
\varepsilon' = \frac{Ct}{\varepsilon_0 A} \quad \text{and} \quad \varepsilon'' = \frac{\sigma'(\omega)}{\varepsilon_0 \omega} \tag{3.8}
\]

where, \( t \) is the sample thickness, \( A \) is the cross-sectional area, \( \sigma'(\omega) \) is the real part of ac conductivity, and \( \varepsilon_0 \) is the permittivity of free space. The spectroscopic plot of the real part of the complex permittivity, \( \varepsilon^*(\omega) \) of \( \text{Li}_{1.3}\text{Ti}_{1.7}\text{Al}_{0.3} \text{PO}_4 \times \text{VO}_4 \times \text{PO}_4 \) shows relaxation at the high frequency. This results from the constriction effect at the grain-boundaries [35] and is explicit in the impedance representation. This relaxation is prominent in the samples milled for longer times since the grain-boundaries are more significant in those samples [36].
The $\varepsilon'$ of Li$_{1.3}$Ti$_{1.7}$Al$_{0.3}$(PO$_4$)$_{2.9}$(VO$_4$)$_{0.1}$ material shows a prominent increase at low frequency which is associated with charges accumulating at the blocking electrode and can be seen in Fig. 3.9(a). Permittivity loss in the 55h ball-milled material shows an order of magnitude increase in comparison to the microcrystalline material as shown in Fig. 3.9(b). The augmented permittivity loss may be due to the ease of diffusion through the grain-boundaries that is reflected in the total conductivity hike of the 55h ball-milled material.

![Figure 3.9: Frequency dependence of (a) real part of the permittivity at different temperatures of 55h ball-milled Li$_{1.3}$Ti$_{1.7}$Al$_{0.3}$(PO$_4$)$_{2.9}$(VO$_4$)$_{0.1}$ material and (b) permittivity loss of microcrystalline and 55h ball-milled Li$_{1.3}$Ti$_{1.7}$Al$_{0.3}$(PO$_4$)$_{2.9}$(VO$_4$)$_{0.1}$ material at 65°C.](image)

### 3.3.2.3 Modulus Representation

An alternative approach to explore the electrical relaxation in ion conducting materials is the complex electric modulus, $M^*(\omega)$ formalism. The real part, $M'$ and the imaginary part, $M''$ of the complex modulus, $M^*(\omega)$, are calculated from $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ using Eq. (2.21). Effects of electrode polarization are suppressed in the modulus representation due to its insensitiveness to the polarization process. These polarization processes are characterized by capacitances values, which are much larger than the grain capacitance and modulus representation is inversely proportional to the capacitance values. Non-Debye behaviour of conductivity relaxation is reflected in the broad maximum of $M''(\omega)$. In Fig. 3.10, the imaginary part 55h ball-milled Li$_{1.3}$Ti$_{1.7}$Al$_{0.3}$(PO$_4$)$_{2.9}$(VO$_4$)$_{0.1}$ material shows two maxima as the capacitance contributions from grain and grain-boundary differ by only an order of magnitude in this material. The modulus plot corroborates findings from the impedance and
permittivity formalisms in Li$_{1.3}$Ti$_{1.7}$Al$_{0.3}$(PO$_4$)$_{2.9}$(VO$_4$)$_{0.1}$ material at different temperatures.

![Graph](image-url)

**Figure 3.10:** Frequency dependence of the imaginary part of the complex modulus of 55h ball-milled Li$_{1.3}$Ti$_{1.7}$Al$_{0.3}$(PO$_4$)$_{2.9}$(VO$_4$)$_{0.1}$ material at different temperatures.

### 3.3.2.4 Ac conductivity Behaviour and Scaling Analysis

Fig. 3.11 illustrates the log–log plot of frequency dependence of ac conductivity. In ac dispersive spectrum, the low frequency dc plateau region is followed by power law dependence at high frequencies. Random diffusion of the ionic charge carriers via activated hopping gives rise to frequency-independent dc plateau. Above the characteristic cross-over frequency, conductivity increases with increase in frequency, which indicates the onset of a relaxation mechanism. Dispersion in conductivity occurs when the carriers are not free to move throughout the sample but it hops around the lattice imperfections. This relaxation mechanism is analyzed in the frame work of a power law model using universal dielectric response. Almond and West [37] proposed the following power law expression to describe the real part of bulk ac conductivity:

$$\sigma'(\omega) = \sigma_{dc} \left[ 1 + \left( \frac{\omega}{\omega_p} \right)^n \right]$$

(3.9)

where, $\sigma_{dc}$ is the dc conductivity and $\omega_p$ is the cross-over frequency from dc to dispersive part. The frequency exponent $n$ is related to the degree of correlation among moving ions and its value is found to be between 0.6 and 1 for ion conducting materials [38]. This expression has been used to describe the conductivity behavior below microwave region. The transition region from dc to ac conductivity shifts to
higher frequencies with increase in temperature. In LiTi$_2$(PO$_4$)$_3$, real part of ac conductivity versus frequency at different temperatures shows two dispersive regions in corroboration with the impedance representation. The low frequency part corresponds to the contribution from the grain-boundary and the high frequency part corresponds to grain contribution.

The study of conductivity spectra of several materials at different temperatures leads to a scaling law as in Eq. (2.26). Different frequency scaling parameters have been used to accommodate the diverse physical parameters that vary with sample. The present study uses Ghosh et al., formalism for conductivity scaling of Li$_{1.0}$Ti$_{1.7}$Al$_{0.4}$(PO$_4$)$_{2.88}$(VO$_4$)$_{0.12}$ and Li$_{1.6}$Al$_{0.2}$Ti$_{1.7}$(PO$_4$)$_{2.94}$(VO$_4$)$_{0.06}$ as shown in Fig. 3.12.

**Figure 3.11:** Frequency dependence of ac conductivity of microcrystalline LiTi$_2$(PO$_4$)$_3$ at different temperatures.

**Figure 3.12:** Isotherms of real part of conductivity, $\sigma'(\omega)$, scaled using Ghosh formalism for (a) microcrystalline Li$_{1.0}$Ti$_{1.7}$Al$_{0.4}$(PO$_4$)$_{2.88}$(VO$_4$)$_{0.12}$ and (b) 22h ball-milled Li$_{1.6}$Al$_{0.2}$Ti$_{1.7}$(PO$_4$)$_{2.94}$(VO$_4$)$_{0.06}$ material.
In both these samples, grain-boundary contributions dominate the real part of conductivity. Ghosh scaling approaches satisfy the time-temperature superposition principle except in the low frequency region. Low frequency region in the real part of conductivity is complicated by electrode polarization, where electrical relaxation processes are different from that of grain-boundary region.

3.4 Conclusions

The present chapter describes the effect of high energy ball-milling on structural and electrical properties of NASICON type materials. With this purpose, microcrystalline LiTi$_2$(PO$_4$)$_3$ and LATPV series materials are synthesized by conventional solid-state reaction. The nanocrystalline materials of different crystallite sizes are synthesized by controlling the duration of ball-milling. Electrical properties of the microcrystalline and nanocrystalline materials are studied over a wide range of temperature and frequency. Impedance spectroscopy tool is used to obtain the equivalent circuit, thus separating the grain and grain-boundary contributions. LiTi$_2$(PO$_4$)$_3$ and Li$_{1.3}$Al$_{0.3}$Ti$_{1.7}$(PO$_4$)$_{2.9}$(VO$_4$)$_{0.1}$ show increase in the grain/grain-boundary conductivity with milling durations. Increased conductivity is due to the feasible conduction through grain-boundaries because milling introduces defects like grain-boundaries in the system. The reduction in the crystallite size due to milling increases the volume fraction of grain-boundaries, which represent easier paths for ion diffusion. The manifestation of grain-boundaries can be seen clearly in the spectra of complex impedance, permittivity and modulus data of 55h ball-milled Li$_{1.3}$Ti$_{1.7}$Al$_{0.3}$(PO$_4$)$_{2.9}$(VO$_4$)$_{0.1}$ material. But this is not evident in microcrystalline and 22h ball-milled material because of the less volume fraction of grain-boundaries. The present study clearly demonstrated and explained that the grain-boundary played a major role in ion diffusion in nanocrystalline materials.

Other members of the LATPV series, Li$_{1.0}$Al$_{0.4}$Ti$_{1.7}$(PO$_4$)$_{2.88}$(VO$_4$)$_{0.12}$ and Li$_{1.6}$Al$_{0.2}$Ti$_{1.7}$(PO$_4$)$_{2.94}$(VO$_4$)$_{0.06}$ were synthesized in the microcrystalline and nanocrystalline form. The stoichiometric mixture is ball-milled for different durations to obtain nanocrystallites of various sizes. Lattice parameters increase and crystallite size decreases with milling durations. In LATPV series, the material that is ball-milled for 55h shows both grain and grain-boundary contributions in the frequency window. Even though, the crystallite size decreased with ball-milling, Li$_{1.0}$Al$_{0.4}$Ti$_{1.7}$(PO$_4$)$_{2.88}$(VO$_4$)$_{0.12}$ and Li$_{1.6}$Al$_{0.2}$Ti$_{1.7}$(PO$_4$)$_{2.94}$(VO$_4$)$_{0.06}$ did not show
consistent increase in dc conductivity. In Li$_{1.0}$Al$_{0.4}$Ti$_{1.7}$(PO$_4$)$_{2.88}$(VO$_4$)$_{0.12}$, 44h ball-milled material shows less conductivity than microcrystalline material. From these observations, it is concluded that ball-milling technique is to be optimized to obtain the consistent results. The grain conductivity values of the microcrystalline material synthesised in the present study differ from the reported values because of the air sintering and different sintering temperatures used in this study.
References


