AC conductivity and dielectric studies of modified Li$_4$SiO$_4$ ceramic electrolytes

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Abstract

AC conductivity of modified Li$_4$SiO$_4$ (Li$_{3.94}$Cr$_{0.02}$SiO$_4$, Li$_4$Zr$_{0.06}$Si$_{0.94}$O$_4$ and Li$_{3.94}$Cr$_{0.02}$Zr$_{0.06}$Si$_{0.94}$O$_4$) was measured as a function of frequency in the range between 1 Hz to 1000 Hz and in temperature range between 303 K to 773 K. The frequency dependence of conductivity for these ceramic electrolytes followed the universal power law variation, $\sigma_{AC}(\omega) = \sigma_0 + A\omega^s$. The plots of pre-exponent $\sigma_0$ versus temperature of all systems suggested that the conduction mechanism in all systems can be described using correlated barrier hopping model. Meanwhile, the charge carrier concentration and mobile ion concentration in all samples was found to be constant over the temperature range of this study while mobility of ion increased with temperature implying that the increase in conductivity with temperature was due to the increase in ion mobility. The experimental results also revealed that the dielectric constant and dielectric loss decreased with frequency. The double substituted sample, Li$_{3.94}$Cr$_{0.02}$Zr$_{0.06}$Si$_{0.94}$O$_4$ showed the highest dielectric constant and dielectric loss at low frequencies. The increase in temperature also increased the dielectric constant and dielectric loss values in all samples.

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1. Introduction

Lithium-type lithium orthosilicate, Li$_4$SiO$_4$ offers several advantages over other types of Li$^+$ ion conductors. This compound can be easily synthesized, less expensive to produce, safe, stable in air, no reaction with lithium metal, low self-discharge, and maintains its conductivity (constant conductivity) with time [1]. This compound also shows favorable characteristics for practical application due to its superior incombustibility, high energy density and wide electrochemical stability window [2]. Stoichiometric Li$_4$SiO$_4$, which is a poor conductor ($\sigma_{100^\circ C}=10^{-6}$ S cm$^{-1}$) has been modified in order to enhance its conductivity. The modification was done by partial substitution using isovalent or aliovalent cation. The partial substitution of Si$^4+$ with Zr$^4+$ (Li$_4$Zr$_{0.06}$Si$_{0.94}$O$_4$) can enlarge the Li$^+$ migration channel while the substitution of 3Li$^+$ with Cr$^{3+}$ (Li$_{3.94}$Cr$_{0.02}$SiO$_4$) is able to create vacancy sites in Li$_4$SiO$_4$ structure. The studies on these partial substitutions have been recently reported by the authors [3,4]. In fact, the double partial substituted Li$_4$SiO$_4$ using both Cr$^{3+}$ and Zr$^{4+}$ ions (Li$_{3.94}$Cr$_{0.02}$Zr$_{0.06}$Si$_{0.94}$O$_4$) has also been reported [4]. However, the reports focus only on the structural and direct current (DC) conductivity of the compounds.

In this article, the AC conductivity and dielectric behaviour of the modified Li$_4$SiO$_4$ (Li$_{3.94}$Cr$_{0.02}$SiO$_4$, Li$_4$Zr$_{0.06}$Si$_{0.94}$O$_4$ and Li$_{3.94}$Cr$_{0.02}$Zr$_{0.06}$Si$_{0.94}$O$_4$) are presented. Based on Jonscher’s universal power law, the conduction mechanism in all samples was analyzed. Meanwhile, the Almond and West formalism was used to investigate the contribution of the charge carrier concentration and charge carrier mobility on the partially substituted Li$_4$SiO$_4$.
2. Experimental procedure

2.1. Synthesis of Li_{3.94}Cr_{0.02}Zr_{0.06}Si_{0.94}O_{4}, Li_{3.94}Cr_{0.02}SiO_{4} and Li_{4}Zr_{0.06}Si_{0.94}O_{4}

All of the compounds investigated in this work were prepared via citrate sol gel method. For preparation of Li_{3.94}Cr_{0.02}Zr_{0.06}Si_{0.94}O_{4} sample, appropriate amounts of lithium acetate, zirconium(IV) acetate hydroxide and chromium(III) acetate were first dissolved in distilled water. In the case of Li_{3.94}Cr_{0.02}SiO_{4} and Li_{4}Zr_{0.06}Si_{0.94}O_{4}, lithium acetate and chromium(III) acetate and lithium acetate and zirconium(IV) acetate hydroxide were employed, respectively. Solution of citric acid was mixed together to the previously prepared solutions under magnetic stirring. The solutions were later transferred into reflux systems and continuously stirred until homogeneous solutions were formed. Solutions of tetraethyl orthosilicate was then added to these homogeneous solutions. After stirring for 12 h, the solutions were taken out and vaporized for about 2 h under magnetic stirring at 75°C. The resulting sticky wet gels formed were dried in an oven at 150°C for 24 h. The obtained powders were ball milled for 24 h using a Fritsch Pulverisette-7 ball mill operated at 500 rpm. The powders were sintered at temperature of 800°C for 12 h and later pressed using a Specac pellet press to form pellets with diameter and thickness of 13 mm and 2.0 mm.

2.2. Characterization techniques

AC conductivity has been evaluated from dielectric data in accordance with the relation:

\[ \sigma_{AC} = \omega e_r e'' \tan \delta \]  

(1)

where \( e_r \) is the permittivity of the free space (8.854 \times 10^{-14} \text{ F cm}^{-1}), \( e'' \) is the dielectric loss. The real and imaginary parts of permittivity and modulus are calculated from the relation [5,6]:

\[ e^* = e' - je'' \]  

(2)

where:

\[ e' = \frac{Z'}{\omega C_0 (Z'^2 + Z''^2)} \]

and

\[ e'' = \frac{Z''}{\omega C_0 (Z'^2 + Z''^2)} \]

In the above equations, \( Z' \) and \( Z'' \) are the real and imaginary impedances obtained from impedance measurements. The currents (I) can be separated into charging current \( (i\omega e') C_0 V \) and loss current \( (i\omega e'') C_0 V \) as given by the following equation,

\[ I = (i\omega e' + i\omega e'') C_0 V \]  

(3)

By using the relation \( C_0 = \varepsilon_r \varepsilon_0 A/d \) (\( \varepsilon_r \): permittivity in vacuum, \( A \): area of electrode and \( d \): distance between electrode), the current density (J) can be related to the complex admittance \( (Y^*) \) as follows,

\[ J = (i\omega e' + i\omega e'') E = (i\sigma + \sigma') E = Y^* E \]  

(4)

Therefore,

\[ \sigma' = \omega e_r e' \quad \text{and} \quad \sigma'' = \omega e_r e'', \]

(5)

where \( \sigma' \) is loss current conductivity (conductance), also known as AC conductivity \( \sigma_{AC} \) in the present study, and \( \sigma'' \) is the conductivity due to charging current (susceptance). On the other hand, complex admittance \( (Y^*) \) is the inverse of \( Z^* \) [5,7].

3. Result and discussion

3.1. Phase identification

Fig. 1 shows the XRD patterns of the prepared Li_{3.94}Cr_{0.02}Zr_{0.06}Si_{0.94}O_{4}, Li_{4}Zr_{0.06}Si_{0.94}O_{4} and Li_{3.94}Cr_{0.02}Zr_{0.06}Si_{0.94}O_{4}. All compounds were successfully indexed according to monoclinic unit cell in space group \( P2_1/m \) which has been explained by the authors previously in [3] and [4]. Fig. 2 shows the magnified XRD patterns in 2\( \theta \) range 16.50°–17.00° in order to confirm that the \( \text{Cr}^{3+} \) and \( \text{Zr}^{4+} \) ions is in the Li_{4}SiO_{4} lattice structure.
As seen in this figure, the peak from the Li$_{3.94}$Cr$_{0.02}$SiO$_4$ sample shifts to higher diffraction angle meanwhile the peaks from Li$_4$Zr$_{0.06}$Si$_{0.94}$O$_4$ and Li$_{3.94}$Cr$_{0.02}$Zr$_{0.06}$Si$_{0.94}$O$_4$ samples shift to lower diffraction angle compared to the peak from undoped Li$_4$SiO$_4$. This indicates that the Cr$^{3+}$ and Zr$^{4+}$ ions are in the Li$_4$SiO$_4$ lattice structure rather than forming impurities [3,4]. Table 1 shows the lattice parameters of all compound. The value of $V$ in Li$_4$Zr$_{0.06}$Si$_{0.94}$O$_4$ increases by 1.27 Å$^3$ compared to parent compound. Meanwhile the value of $V$ in the Li$_{3.94}$Cr$_{0.02}$SiO$_4$ and Li$_{3.94}$Cr$_{0.02}$Zr$_{0.06}$Si$_{0.94}$O$_4$ decreases by 3.27 Å$^3$ and 1.82 Å$^3$, respectively. The increase and decrease of $V$ are attributed to large atomic size of Zr$^{4+}$ than that of Si$^{4+}$ and the creation of two vacancies site due to substitution of 3Li$^{+}$ with Cr$^{3+}$, respectively.

### 3.2. AC conductivity

The log $\sigma_{AC}$ vs log $\omega$ plots of Li$_{3.94}$Cr$_{0.02}$SiO$_4$, Li$_2$Zr$_{0.06}$Si$_{0.94}$O$_4$ and Li$_{3.94}$Cr$_{0.02}$Zr$_{0.06}$Si$_{0.94}$O$_4$ samples for different temperatures are illustrated in Fig. 3. Each plot consists of a spike in low frequency region, a plateau in intermediate frequency region and high frequency dispersion. At low frequencies, dispersion is observed. This is due to electrode polarization effects. Meanwhile, the intermediate frequency plateau is due to frequency independence of conductivity corresponding to DC conductivity. The highest conductivity is exhibited by the in Li$_{3.94}$Cr$_{0.02}$Zr$_{0.06}$Si$_{0.94}$O$_4$ Samples. The transition from the DC plateau to AC conductivity dispersion region shifts towards higher frequency range when temperature increases. At high frequencies, the conductance spectra at different temperatures converge. This indicates that AC conductivity is independent of temperature at high frequencies. In addition, the observed dispersion of conductivity with frequency is in general agreement with the prediction of the jump relaxation model [5,8,9].

According to the jump relaxation model, which takes into account the Coulomb interaction between mobile ions, the exponent of the power law in Eq. (6) is expressed as [5,8]:

$$s = \frac{\text{backhop rate}}{\text{site relaxation rate}}$$  \hspace{1cm} (6)

The backhop is the backward motion of a hopping ion to its initial site, which is caused by the Coulombic repulsive interaction between mobile ions. The site relaxation is the shift of a site potential minimum to the position of the hopping ion, which is caused by a rearrangement of neighboring ions. The decrease in $s$ in all modified Li$_4$SiO$_4$ samples (Fig. 4) may be due to the formation of vacant sites and the movement of Li$^{+}$ from one site to another, which in turn reduces the backhop rate and hence decreases $s$.

The conductivity behavior in all samples obeyed the universal power law, $\sigma_{AC}(\omega) = \sigma_0 + A\omega^s$, where $\sigma_0$ is the DC conductivity, $A$ is the pre-exponential factor and $s$ is the power law exponent which represents the degree of interaction between the mobile ion and is less than 1. The value of $s$ shown in Fig. 4 were extracted from the slope of log $\sigma_{AC}(\omega)$ versus log $\omega$. The parameter of $s$ obtained for Li$_{3.94}$Cr$_{0.02}$SiO$_4$, Li$_2$Zr$_{0.06}$Si$_{0.94}$O$_4$ and Li$_{3.94}$Cr$_{0.02}$Zr$_{0.06}$Si$_{0.94}$O$_4$ compounds are 0.64 at room temperature and 0.38 at 773 K and 0.61 at room temperature and 0.22 at 773 K, respectively. This indicates that the frequency dependence of $\sigma_{AC}$ can be explained in terms of correlated barrier hopping (CBH) model. The plots in Fig. 4 can also be fitted to the equations $s = -0.0011 T + 1.0628$, $s = -0.0006 T + 1.0902$ and $s = -0.0008 T + 1.1505$ for Li$_{3.98}$Cr$_{0.02}$SiO$_4$, Li$_2$Zr$_{0.06}$Si$_{0.94}$O$_4$ and Li$_{3.94}$Cr$_{0.02}$Zr$_{0.06}$Si$_{0.94}$O$_4$ respectively.

### Table 1

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$a \pm 0.048$ (Å)</th>
<th>$b \pm 0.009$ (Å)</th>
<th>$c \pm 0.064$ (Å)</th>
<th>$\beta \pm 0.03$</th>
<th>$V$ (Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_4$SiO$_4$ [4]</td>
<td>5.147</td>
<td>6.094</td>
<td>5.293</td>
<td>90.33</td>
<td>166.01</td>
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<tr>
<td>Li$<em>{3.94}$Cr$</em>{0.02}$SiO$_4$ [4]</td>
<td>5.249</td>
<td>6.079</td>
<td>5.100</td>
<td>90.25</td>
<td>162.74</td>
</tr>
<tr>
<td>Li$<em>2$Zr$</em>{0.06}$Si$_{0.94}$O$_4$ [3]</td>
<td>5.308</td>
<td>6.114</td>
<td>5.155</td>
<td>90.25</td>
<td>167.28</td>
</tr>
<tr>
<td>Li$<em>{3.94}$Cr$</em>{0.02}$Zr$<em>{0.06}$Si$</em>{0.94}$O$_4$ [3]</td>
<td>5.271</td>
<td>6.090</td>
<td>5.114</td>
<td>90.25</td>
<td>164.19</td>
</tr>
</tbody>
</table>

Fig. 3. Conductivity spectra for (a) Li$_{3.94}$Cr$_{0.02}$SiO$_4$ (b) Li$_2$Zr$_{0.06}$Si$_{0.94}$O$_4$ and (c) Li$_{3.94}$Cr$_{0.02}$Zr$_{0.06}$Si$_{0.94}$O$_4$.
calculated using Eq. 9 and \( k \) is the Boltzmann constant. The ionic mobility, \( \mu \) can be calculated using equation:  
\[
\mu = \frac{\sigma_{dc}}{ne}
\]  
\[ (10) \]

The values of \( \omega_p, K, n \) and \( \mu \) for Li\(_{3.94}\)Cr\(_{0.02}\)SiO\(_4\), Li\(_{4}\)Zr\(_{0.06}\)Si\(_{0.94}\)O\(_4\) and Li\(_{3.94}\)Cr\(_{0.02}\)Zr\(_{0.06}\)Si\(_{0.94}\)O\(_4\) samples at various temperatures are listed in Table 2. The table reveals that the charge carrier concentration, \( K \) and mobile ion concentration, \( n \) are constant over the temperature range studied. This implies that all the lithium ions which are responsible for the conductivity are in mobile state thus can be best represented by the strong electrolyte model [8,9,15,18]. The higher conductivity observed for Li\(_{3.94}\)Cr\(_{0.02}\)Zr\(_{0.06}\)Si\(_{0.94}\)O\(_4\) is due to high mobile ion concentration (~10\(^{26}\)) compared to that (~10\(^{25}\)) observed for both Li\(_{3.94}\)Cr\(_{0.02}\)SiO\(_4\) and Li\(_{4}\)Zr\(_{0.06}\)Si\(_{0.94}\)O\(_4\) samples.

Meanwhile, the mobility of ions, \( \mu \) increases with increase in temperature in all samples. This proves that the increase in conductivity with increasing temperature in the samples can be attributed to the increase in ionic mobility or hopping rate since the density of mobile ions is constant over the temperature range chosen for this study [8,9,17].

### 3.3. Frequency dependence of dielectric constant

Fig. 5 illustrates the variation of the dielectric constant, \( \varepsilon' \) with composition at different frequencies for all samples at room temperature. From the figure, it is clear that the dielectric constant decreases with increase in frequency. The double substituted compound, Li\(_{3.94}\)Cr\(_{0.02}\)Zr\(_{0.06}\)Si\(_{0.94}\)O\(_4\) exhibits the highest \( \varepsilon' \) compared to other compounds at all frequencies except 1000 Hz. At low frequencies, the large amount of charge carriers in this compound gives high contribution of charge carrier accumulation at the interface of electrode and hence increases the value of \( \varepsilon' \). When frequency increases, due to high periodic reversal of the field, the contribution of charge carriers towards dielectric constant decreases and reaches a value which is about the same to the value of Li\(_{3.94}\)Cr\(_{0.02}\)SiO\(_4\) and Li\(_{4}\)Zr\(_{0.06}\)Si\(_{0.94}\)O\(_4\) compounds at 1000 Hz [5,13,14,19–21].

Meanwhile, the dielectric constant in all samples increases with temperature (Fig. 6). The increase of \( \varepsilon' \) with temperature can be attributed to the fact that at low temperature, most of the charge carriers cannot orient themselves with respect to the direction of the applied field giving a weak contribution to the polarization and \( \varepsilon' \). When temperature increases, the charge carriers acquire sufficient excitation thermal energy and are able to rotate more easily to obey the change in external field. This in turn increases their contribution to the polarization leading to an increase in \( \varepsilon' \) [5,13,14,19–21].

### 3.4. Frequency dependence of dielectric loss

The variation of the dielectric loss, \( \varepsilon'' \) with composition at different frequencies for all samples at room temperature is shown in Fig. 7. As seen in this figure, the \( \varepsilon'' \) decreases with increase in frequency. At low frequencies (1 Hz and 10 Hz),
the higher migration rate causes greater loss of energy to the lattice as heat and is reflected by higher value of $\varepsilon''$. Meanwhile, at high frequencies (100 Hz and 1000 Hz), all sample show the same value of $\varepsilon''$. This is because at these frequencies, ion vibration may be the only source of dielectric loss and as a consequence the values of $\varepsilon''$ are more or less the same for all samples [22,23]. However, $\varepsilon''$ increases with temperature as shown in Fig. 8. The increase in dielectric loss with temperature is attributed to an increase of ion migration rate. This is due to increase mobility of ions as shown in Table 2.

4. Conclusions

The AC conductivity of the compound studied in this work obeyed the universal power law and can be described using the CBH model. The conductivity parameters such as hopping frequency, charge carrier concentration and mobile ion

<table>
<thead>
<tr>
<th>Samples</th>
<th>$T$ (K)</th>
<th>$\omega_p$ (MHz)</th>
<th>$K$ (S cm$^{-1}$ kHz$^{-1}$)</th>
<th>$n$ (cm$^{-3}$)</th>
<th>$\mu$ (cm$^2$ V$^{-1}$ s$^{-1}$)</th>
</tr>
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<tr>
<td>Li$<em>4$Zr$</em>{0.06}$Si$_{0.94}$O$_4$</td>
<td>303</td>
<td>1.531</td>
<td>$6.72 \times 10^{-9}$</td>
<td>$4.02 \times 10^{25}$</td>
<td>$5.27 \times 10^{-12}$</td>
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<tr>
<td></td>
<td>373</td>
<td>1.970</td>
<td>$6.72 \times 10^{-9}$</td>
<td>$4.02 \times 10^{25}$</td>
<td>$5.52 \times 10^{-12}$</td>
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<tr>
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<td>473</td>
<td>2.630</td>
<td>$6.74 \times 10^{-9}$</td>
<td>$4.03 \times 10^{25}$</td>
<td>$6.85 \times 10^{-12}$</td>
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<td>3.755</td>
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<td>$7.28 \times 10^{-11}$</td>
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<td>0.548</td>
<td>$1.38 \times 10^{-8}$</td>
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<td>Li$<em>3$Si$</em>{0.02}$Cr$<em>{0.02}$Zr$</em>{0.06}$Si$_{0.94}$O$_4$</td>
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<td>$6.56 \times 10^{26}$</td>
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concentration have been calculated by fitting the conductance spectra to the power law variation. Li$_{3.94}$Cr$_{0.02}$Zr$_{0.06}$Si$_{0.94}$O$_4$ showed the highest dielectric constant and dielectric loss compared to Li$_{3.94}$Cr$_{0.02}$SiO$_4$ and Li$_4$Zr$_{0.06}$Si$_{0.94}$O$_4$ compounds at low frequencies. Dielectric constant and dielectric loss of all samples decreased with increase in frequency but increase as temperature increase. The increase of dielectric constant with temperature was due easier orientation of charge carrier to obey change in external field. Meanwhile, the increases of dielectric loss with temperature was attributed to an increase of ion migration rate.

Acknowledgments

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