Citrate sol–gel synthesised Li$_4$SiO$_4$: conductivity and dielectric behaviour

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Pure Li$_4$SiO$_4$ ceramic material is obtained using citrate sol–gel method followed by sintering at 750°C. The crystallographic phase of the material is investigated by X-ray diffraction. The conductivity of the ceramic material is determined at different temperatures. Meanwhile, the dielectric properties are observed in order to obtain further information on ion dynamics in the material. The X-ray diffraction result shows the formation of a pure monoclinic Li$_4$SiO$_4$ crystal structure with lattice parameters $a=5.140$ Å, $b=6.094$ Å, $c=5.293$ Å and $\beta=90^\circ$. The conductivity of the material increases linearly with the increase in temperature. The conductivity of the sample is $1.16 \times 10^{-4}$ S cm$^{-1}$ at 100°C. The frequency dependence of conductivity follows the universal power law variation $\sigma_{ac}(\omega)=\sigma_0+A\omega^s$. The plot of pre-exponent $s$ versus temperature suggests that the conduction mechanism in the system can be described using correlated barrier hopping model. The increase in dielectric constant and dielectric loss and the peak shift of tan $\delta$ to higher frequencies with temperature indicate that the increase in conductivity with temperature is due to the increase in number and hopping rate of charge carriers with temperature.

Keywords: Ceramic, Conductivity, Dielectric, Solid electrolyte, Sol-gel

Introduction

In the search of electrolytes for a variety of solid state devices and batteries with Li$^+$ ion conductors, systems based on lithium orthosilicate, Li$_4$SiO$_4$ have been considered. Li$_4$SiO$_4$ is a ceramic material with appreciable cationic conductivity. This compound has a versatile host structure and can form non-stoichiometric materials by doping with different cations, such as Zn$^{2+}$ to form lithium super ionic conductor materials. The cations replace lithium ions in tetrahedral sites, while the additional lithium ions occupy interstitial octahedral sites. Their concentration is the main factor determining the conductivity of these solid electrolytes.

The crystal structure of Li$_4$SiO$_4$, which has a tetragonal packed arrangement, is complex. Some crystals appear to contain lithium ions in partially occupied four-, five- and six-coordinate sites. Other crystals possess a large supercell in which the various four-, five- and six-coordinate sites are fully occupied. Because of the large number of lithium sites in the unit cell of the (LiO$_4$) polyhedral, where $n=4,5,6$, they are often linked together by sharing common faces. There are six distinct sets of sites occupied by lithium with occupancy factors ranging from 1/3 to 2/3.

Li$_4$SiO$_4$ can be synthesised using conventional solid state reaction method. However, this method involves high heating temperature and yields samples with low conductivity ($\sigma_{20^\circ}^C=10^{-2}$ S cm$^{-1}$). The sol–gel technique is an alternative method for preparing this compound. This technique has the advantages of lowering the synthesis temperature and improving grain boundary conductivity and is a high purity process that is expected to produce samples with higher conductivity.

The work reported in this article is dedicated to obtaining Li$_4$SiO$_4$ material via the citrate sol–gel method in the hope of obtaining Li$_4$SiO$_4$ samples with higher conductivity. Dielectric studies are also performed in order to understand the ion dynamics in the samples.

Experimental

Synthesis of samples

For the preparation of Li$_4$SiO$_4$ powder, Li$_2$O and SiO$_2$ are used as starting materials, while citric acid (C$_6$H$_8$O$_7$) is used as chelating agent. The molar ratio of Li$_2$O/SiO$_2$ is fixed at 4:1 based on the stoichiometric formula of Li$_4$SiO$_4$. Li$_2$O is dissolved in distilled water before mixing with SiO$_2$ and citric acid, which is used to adjust the pH value of the solution to alkali (pH=8-5). The mixture is then stirred under continuous reflux process for 1 h until a colloidal solution is obtained. The colloidal solution is vapoured at 80°C, and a gel is formed ultimately. The gel is dried at 150°C for 24 h to remove H$_2$O and residual organic groups and also to avoid ceramic cracks. The obtained powder is pelletised, and the pellets formed are later sintered at different temperatures, from 600 to 750°C for 4 h. The sintered pellets for the ac conductivity measurements are 13 mm in diameter and 2 mm in thickness.
Characterisation of samples

Crystallographic phases present in the prepared samples are identified by X-ray diffraction (XRD) using a Bruker AXS X-Ray diffractometer with Cu Kα radiation. Complex impedance parameters (i.e., impedance and phase angle parameters) are measured with a computer controlled Solatron 1260 impedance analyser with platinum as the blocking electrode in the temperature range from 25 to 100 °C over a frequency range from 0-1 to 10⁶ Hz. The ac conductivity has been evaluated from dielectric data in accordance with the relation

\[ \sigma' = \omega \varepsilon_0 \varepsilon'' \tan \delta \]  

(1)

where \( \varepsilon_0 \) is the permittivity of free space (8.854 \times 10^{-14} \text{ F cm}^{-1}), \tan \delta \) is the tangent loss factor and \( \varepsilon'' \) is the dielectric loss. The real and imaginary parts of permittivity and modulus are calculated from the relation

\[ \varepsilon'' = \varepsilon' - j \varepsilon'' \]  

(2)

where

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

and

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

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

\[ I = (j \omega \varepsilon' + j \omega \varepsilon'')C_0 V \]  

(3)

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

\[ J = (j \omega \varepsilon' + j \omega \varepsilon'')E = (j \sigma' \varepsilon'' + \sigma'')E = Y^* E \]  

(4)

Table 1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>( a, \text{ Å} )</th>
<th>( b, \text{ Å} )</th>
<th>( c, \text{ Å} )</th>
<th>( V, \text{ Å}^3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Present Work</td>
<td>5.147</td>
<td>6.094</td>
<td>5.293</td>
<td>166.01</td>
</tr>
<tr>
<td>Dubey and West</td>
<td>5.140</td>
<td>6.100</td>
<td>5.300</td>
<td>166.17</td>
</tr>
</tbody>
</table>

Results and discussion

Phase identification

Presented in Fig. 1 are the XRD spectra of Li₄SiO₄ sintered at different temperatures for 4 h. As can be observed in the figure, the samples sintered at 600–700 °C exhibited sharp diffraction peaks attributed to Li₄SiO₄ and Li₂CO₃, indicating the presence of both compounds in the samples. The XRD spectrum of the sample sintered at 750 °C shows peaks attributed only to Li₄SiO₄, demonstrating that pure Li₄SiO₄ has been obtained.

The pure Li₄SiO₄ compound is found to be single phase in nature, crystallising in monoclinic structure with the space group P2₁/m. The lattice parameters are listed in Table 1. The parameters are in good agreement with the values reported by Dubey and West.

Conductivity measurement

Direct current conductivity

Illustrated in Fig. 2 are the impedance spectra of the samples sintered at 750 °C (pure Li₄SiO₄ samples) recorded at room temperature (RT) and 100 °C. The spectra consist of two depressed semicircles in the high frequency region followed by a spike in the low frequency region. The bulk resistance \( R_b \) is determined from the intercept at the real impedance axis of the first semicircle. The dc conductivity value of the bulk conductivity is calculated using the equation

\[ \sigma_b = \frac{d}{AR_b} \]  

(6)

where \( d \) is the sample thickness, \( A \) is the area of the electrode and \( R_b \) is the bulk resistance.

The dc ionic conductivities for the sample sintered at 750 °C from complex impedance plots for different temperatures are analysed by the Arrhenius equation

\[ \sigma_b T = A \exp \left( -\frac{E_a}{RT} \right) \]  

(7)

where \( A \) is the pre-exponential factor, \( E_a \) is the activation energy for conduction and \( k \) is the gas constant. Figure 3 depicts the Arrhenius plot for the sample. It is observed that the conductivity increases with the increase in temperature. The conductivity of the sample is determined to be 3.36 \times 10^{-6} \text{ S cm}^{-1} \text{ at RT and } 1.16 \times 10^{-4} \text{ S cm}^{-1} \text{ at 100 °C. The conductivity value at 100 °C is an order of magnitude higher compared to the value reported by Smith et al. measured at the same temperature.}
The linear plot in Fig. 3 suggests that there are no structure and phase changes in the sample for the studied temperature range. The activation energy of the sample is determined from the gradient of the Arrhenius plot. The activation energy normally includes energy for the formation and migration of ions. According to West, the Li$_4$SiO$_4$ structure is in the extrinsic regime below 200°C. In this extrinsic regime, the activation energy is dominated by the migration energy. The activation energy $E_a$ determined from the slope of log $\sigma_d$ versus $1000/T$ plot is 0.19 eV. The low value of activation energy indicates high mobility of ions in the sample.

**Alternating current conductivity**

The log $\sigma_{ac}$ versus log $\omega$ plots of the pure Li$_4$SiO$_4$ samples for different temperatures are shown in Fig. 4. The plots consist of three regions, i.e. a spike in the low frequency region, an intermediate frequency plateau and a high frequency dispersion. The dispersion in the ac conductivity at low frequencies arises from electrode polarisation. At these frequencies, the ionic conductivity is high enough to produce a significant build-up of charges at the electrodes, which reduces the effective applied field across the sample and hence the apparent conductivity.

At the plateau region, the conductivity is frequency independent, and the value of conductivity at this plateau region agrees well with the dc conductivity determined from impedance plots. The switch over from the frequency independent region to the frequency dependent region signals the onset of conductivity relaxation, which shifts towards higher frequencies as the temperature increases. The observed dispersion of conductivity with frequency is in general agreement with the prediction of the jump relaxation model. According to this model, at very low frequencies ($f \to 0$), an ion can jump from one site to its neighbouring vacant site successfully contributes to dc conductivity. At high frequencies, the probability for the ion to jump back to its initial site increases due to the short time periods available. The high probability for the correlated forward backward hopping at high frequencies together with the relaxation of the dynamic cage potential is responsible for the high frequency dispersion.

The conductivity behaviour obeys the universal power law $\sigma_{ac}(\omega)=\sigma_{dc} A \omega^s$, where $\sigma_{dc}$ is the dc conductivity, $A$ is the pre-exponential factor and $s$ is the fractional exponent. The value of $s$ is extracted from the slope of log $\sigma_{ac}(\omega)$ versus log $\omega$. The parameter of $s$ obtained varies from 0.70 at RT and decreases to 0.09 at the highest temperature of 373 K. This indicates that the frequency dependence of $\sigma_{AC}$ can be explained in terms of this law. The plot of variation of $s$ with temperature is illustrated in Fig. 5. The plot can also be fitted to the equations $s=-0.0077T+1.0778$. This equation suggests that $s \to 1$ when $T \to 0$.
The frequency exponent $s$ in the Correlated Barrier Hoping (CBH) model is in the range from 0 to 1 at RT and decreases with increasing temperature and can be evaluated as follows:

$$s = 1 - \frac{6kT}{W_M}$$

where $k$ is Boltzmann’s constant, $T$ is the temperature and $W_M$ is the maximum barrier height. From equation (8), it can be deduced that $s \rightarrow 1$ if $T \rightarrow 0$. This confirms that the conduction mechanism in the Li$_4$SiO$_4$ system studied in this work can be described using the CBH model.

According to the correlated barrier hopping model, it is assumed that the ions or charge carriers are surrounded by several potentials, such as the Coulombic repulsive potential between the ions and a potential well in which the ions reside. Superposition of the potentials yields a single ion potential that is actually felt by the ions. When the ion gains sufficient energy, they hop from one site to another. As the temperature increases, the number of ions that hop from one site to another increases, leading to an enhancement in conductivity with temperature, as observed in Fig. 4.

### Dielectric Study

In order to obtain further information on the ion dynamic properties in the Li$_4$SiO$_4$ material, its dielectric properties are studied. Figure 6 shows the frequency dependence of dielectric constant $\varepsilon'$ at different temperatures for the material. From the figure, it can be seen that the value of $\varepsilon'$ decreases to a constant value with frequency but increases with temperature. The low frequency is attributed to the contribution of charge carrier accumulation at the interface of the electrode and the Li$_4$SiO$_4$ material. At high frequencies, due to the high periodic reversal of the field, the contribution of charge carriers towards dielectric constant decreases with frequency. Meanwhile, the increase in $\varepsilon'$ with temperature can be attributed to the fact that at low temperature, the charge carriers on most cases cannot orient themselves with respect to the direction of the applied field; thus, they possess a weak contribution to polarisation and $\varepsilon'$. When the temperature is increased, the bound charge carriers get sufficient excitation thermal energy to be able to obey the change in external field more easily. This in turn increases their contribution to polarisation, resulting in an increase in $\varepsilon'$.22

Figure 7 depicts the frequency dependence of dielectric loss $\varepsilon''$ at different temperatures for the Li$_4$SiO$_4$ material. From the figure, $\varepsilon''$ decreases with frequency and increases with temperature. The decrease of $\varepsilon''$ with frequency can be attributed to the fact that at low frequencies, the electrical energy loss is high due to the migration of ions in the material. As the ion moves, they lose some of their energy to the lattice as heat, and so $\varepsilon''$ has high value. Meanwhile, at moderate frequencies, $\varepsilon''$ is due to the mix contribution of ion jump, conduction loss of ions migration and ion polarisation loss. At high frequencies, ion vibrations may be the only source of dielectric loss, and as a consequence, $\varepsilon''$ has minimum value.25 The increase in dielectric loss with temperature may be attributed to an increase of conduction processes arising from thermally generated charge carriers.25–26

The dielectric loss factor is the phase difference due to the loss of energy within the sample at a particular frequency.

5 Value for $s$ for Li$_4$SiO$_4$ material at different temperatures

The frequency exponent $s$ in the Correlated Barrier Hoping (CBH) model is in the range from 0.7 to 1 at RT and decreases with increasing temperature and can be evaluated as follows:

$$s = 1 - \frac{6kT}{W_M}$$

where $k$ is Boltzmann’s constant, $T$ is the temperature and $W_M$ is the maximum barrier height. From equation (8), it can be deduced that $s \rightarrow 1$ if $T \rightarrow 0$. This confirms that the conduction mechanism in the Li$_4$SiO$_4$ system studied in this work can be described using the CBH model.

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frequency and is expressed as $\tan \delta = \frac{\varepsilon''}{\varepsilon'}$. Figure 8 presents the plot of frequency dependence of $\tan \delta$ at various temperatures. The plot shows a peaking behaviour for all temperatures. As the temperature increases, the $\tan \delta$ peak is shifted towards higher frequency. The shift of peak of $\tan \delta$ towards higher frequency with the increase in temperature suggests that the ion jumping probability increases with increasing temperature.22,26

Conclusions

Pure Li$_4$SiO$_4$ compound has been successfully obtained via citrate sol–gel method. The dc conductivity of the Li$_4$SiO$_4$ compound increases with temperature. The conductivity is in the order of $10^{-4}$ S cm$^{-1}$ at 100°C. The ac conductivity obeys the universal power law and may be described using the CBH model. The dielectric study shows that the increase in conductivity is ascribed to the increase in number as well jumping rate of charge carriers as reflected by the increase in dielectric constant and the shift of $\tan \delta$ peak towards higher frequency as the temperature is increased.

References