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Effect of Cr^{3+} Substitutions on Conductivity of $Li_{4.08+y}Zn_{0.04}Cr_ySi_{0.96-y}O_4$ ($0.01 \leq y \leq 0.03$) Ceramic Electrolytes at High Temperature

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The objective of the present study was to investigate the effect of Cr^{3+} substitutions on conductivity of $Li_{4.08+y}Zn_{0.04}Cr_ySi_{0.96-y}O_4$ ($0.01 \leq y \leq 0.03$) prepared via sol gel method. X-ray diffraction was applied to investigate the crystalline phase, structure and unit cell parameters of those solid electrolytes. Complex impedance spectroscopy was carried out to study the Li^+ conductivity. The result showed that the $Li_{4.08+y}Zn_{0.04}Cr_ySi_{0.96-y}O_4$ with $y = 0.03$ exhibited highest total conductivity of 6.27×10^{-5} S cm^{-1} at 473 K and 2.44×10^{-3} S cm^{-1} at 773K. The insertion of Cr^{3+} found to enhance conductivity as a result of increase in Li^+ ion concentration and mobility.

Keywords: Arrhenius, ceramic electrolytes, conductivity, LISICON

1. INTRODUCTION

Lithium Orthosilicate, Li_4SiO_4 is one of the LISICON group members which have attract research interest because of their easily synthesized, less expensive to produce, stable in air, low self discharge and no reaction with lithium metal [1]. The basic structure of Li_4SiO_4 is monoclinic and composed of hexagonal close packed oxygen ion arrays which is iso-structural with γ-Li_3PO_4. The SiO_4 and LiO_4 tetrahedral share oxygen vertices to form a loose three-dimensional framework favourable for ion transport. The lithium ion diffusion is expected to occur through tetrahedral site and interstitial octahedral site pathway [2-3].

For the past 10 years, great efforts have been made for enhancing the Li^+ conductivity in Li_4SiO_4 compound. Many attempts have been reported in the literature. Double partial substitutions using Cr^{3+} and Zr^{4+} with the formula of $Li_{4-3x}Cr_xZr_ySi_{1-y}O_4$ with $x = 0.02$ and $y = 0.06$ has been reported by authors previously enhanced the conductivity of Li_4SiO_4 compound by two orders of magnitude [2]. Meanwhile, partials substitutions using different cations also have been reported can create extra lithium interstitial in the Li_4SiO_4 structure such as in $Li_{4+x}T_xSi_{1-x}O_4$ ($T = B^{3+}$, Al^{3+}, Ga^{3+}, Cr^{3+}, Fe^{3+}) system [4-7]. The extra lithium interstitial accommodated in the distorted tetrahedrally or octahedrally site leading to an increase of charge carrier concentration in the compound and also giving rise to conductivity. However, the partial substitution on the Si^{4+} site in the Li_4SiO_4 compound using Zn^{2+} and Cr^{3+} which forming compounds with the formula $Li_{4+2x+y}Zn_xCr_ySi_{1-x-y}O_4$ has not been reported previously. Apart of the larger size than Si^{4+}, which is expected to enlarge the migration channel of the structure, the inclusion of Zn^{2+} and Cr^{3+} in the Li_4SiO_4 structure also introduces extra interstitial Li^+ ions. As such, in this study, $Li_{4.08+y}Zn_{0.04}Cr_ySi_{0.96-y}O_4$ with $y = 0.01, 0.02, 0.03, 0.04$ were synthesized by sol gel method and characterized. The effect of double substitutions using Cr^{3+} and Zn^{2+} on the conductivity of Li_4SiO_4 were investigated.

2. EXPERIMENTAL PROCEDURE

2.1 Synthesis of samples

For preparation of the sample, lithium acetate, zinc acetate and chromium(III) acetate and tetraethyl orthosilicate were used as the starting materials while citrate acid was used as the chelating agent. All the chemicals were first dissolved in distilled water with molar ratio of Li : Zn : Cr : Si fixed according to formula $Li_{4+2x+y}Zn_xCr_ySi_{1-x-y}O_4$ ($x = 0.04$, $y = 0.01, 0.02, 0.03, 0.04$). The variable of x was fixed to 0.04 due to the maximum value to obtain pure sample. Solution of citric acid was mixed together to the previously prepared solutions under magnetic stirring. The solutions were transferred into reflux systems and continuously stirred until homogeneous solutions were formed. Solution of tetraethyl orthosilicate was later added to these homogeneous solutions. After stirring for 12 hours, the solutions were taken out and then vaporized for about 2 hours under magnetic stirring at 75^{o}C. The resulting sticky wet gels formed were dried in an oven at 150^{o}C for 24 hours. The powders were sintered at temperature 800^{o}C for 12 hours and later pressed using a Specac hydraulic pellet press to form pellets with diameter and thickness of 13 mm and 2.0 mm.

2.2. Characterization techniques

XRD patterns of the powder samples were recorded using PANalytical-X'pert^3 X-ray Diffraction spectrometer. The samples were subjected to a beam of Cu-K$_\alpha$ radiation of wavelength of 1.5406 Å. The patterns were recorded in 2θ range between 10^o to 70^o at the rate of 0.016^o in step width and analyzed using High score plus software. The conductivity of the samples were determined using Solatron 1260 impedance analyzer over a frequency range from 1 to 10^6 Hz. The samples were sandwiched between two stainless steel electrodes. Meanwhile, the AC conductivity has been calculated from dielectric data in accordance with the relation:

$$\sigma_{AC} = \omega\varepsilon_o\varepsilon'' \tan\delta \qquad (1)$$

where ε_o is permittivity of the free space, ε'' is dielectric loss, ω is $2\pi f$ and $\tan\delta$ is the dielectric loss factor [8].

3. RESULT AND DISCUSSION

3.1 Phase analysis

Displayed in Fig. 1 are XRD patterns of $Li_{4.08+y}Zn_{0.04}Cr_ySi_{0.96-y}O_4$ (y = 0.01, 0.02, 0.03, 0.04) sintered for 12 h at 800°C. The XRD patterns of all samples can be indexed to monoclinic structure in space group $P2_{1/m}$ (with Ref. no : 98-002-5759). The Zn^{2+} and Cr^{3+} could only be substituted with the Si^{4+} without the presence of impurities up to x = 0.04 and y = 0.03. This also suggests that the full substitution of Si^{4+} by Zn^{2+} and Cr^{3+} occurred in the lattice structure of Li_4SiO_4. As such, further analyze was only done on the samples with $0.01 \le y \le 0.03$.

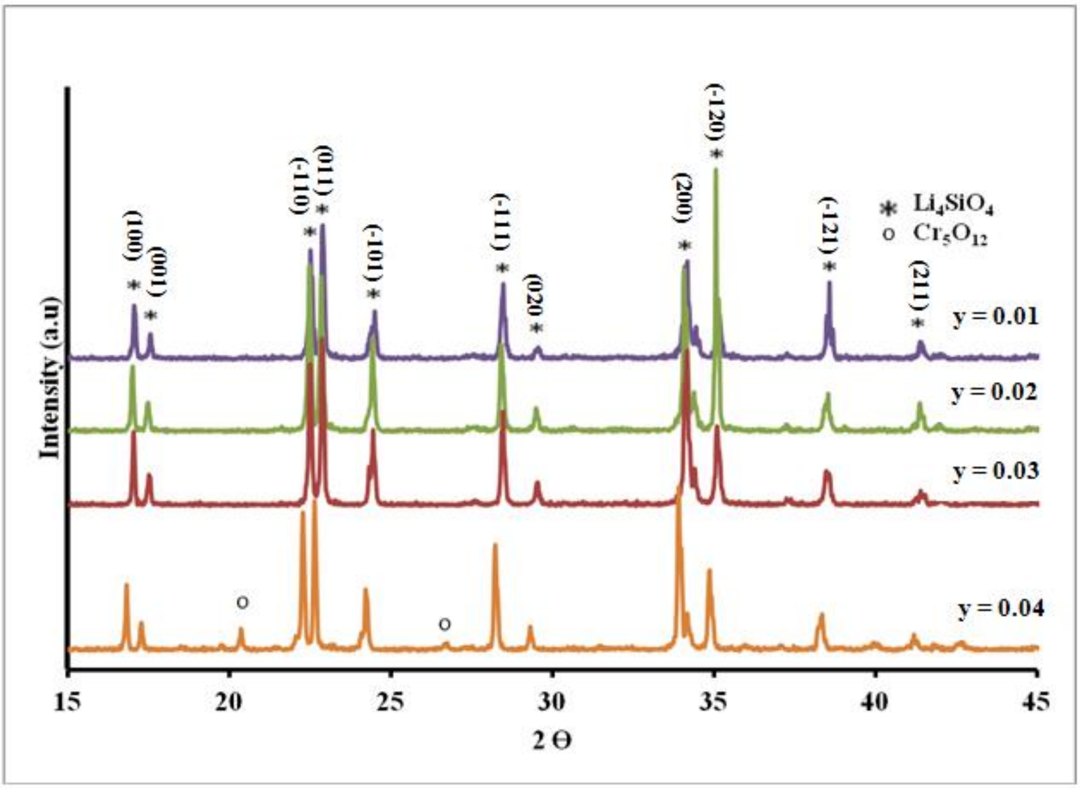

Figure 1. XRD patterns of $Li_{4.08+y}Zn_{0.04}Cr_ySi_{0.96-y}O_4$ samples

Figure 2 shows all peaks at (100) plane which were contributed by the substitutions of Si^{4+} with Cr^{3+} and Zn^{2+} shift to lower diffraction angles compared to the unsubstituted Li_4SiO_4 [9]. This suggests that there are more ions accommodated in the lattice structure. The substitutions of Si^{4+} by Cr^{3+} and Zn^{2+} cause distortion of the hcp sublattices generating tetrahedral packed array due to the difference in the ionic radius of Si^{4+} (0.41 Å) compare to Cr^{3+}(0.64 Å) and Zn^{2+} (0.74 Å). The mechanism allows additional cations to be accommodated in the tetrahedral sites. This is especially advantageous for lithium ions which owing to their small size can be readily accommodated in the distorted tetrahedrally and octahedrally co-ordinated [2].

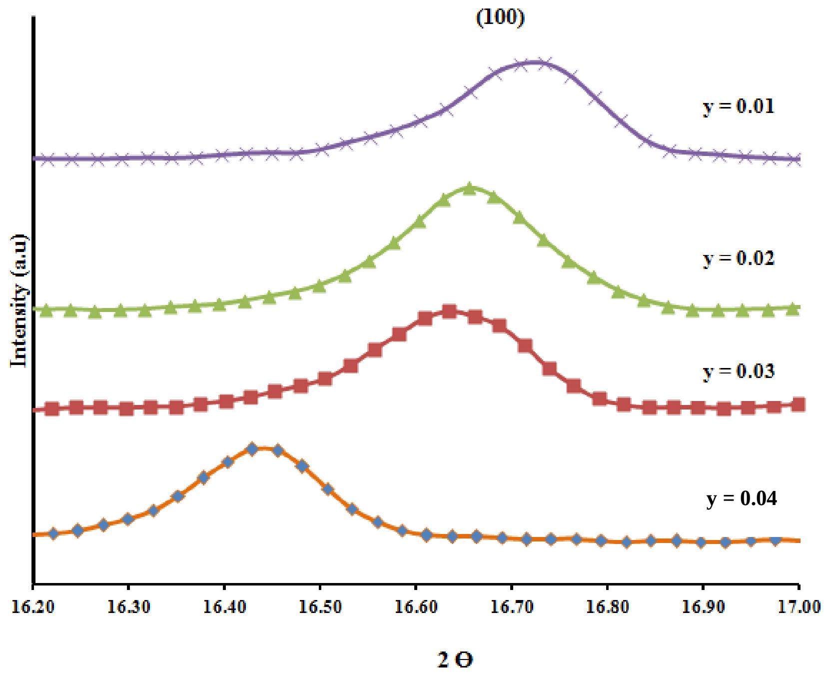

Figure 2. XRD patterns of $Li_{4.08+y}Zn_{0.04}Cr_ySi_{0.96-y}O_4$ samples in 2Θ range from 16.20 to 17.00°

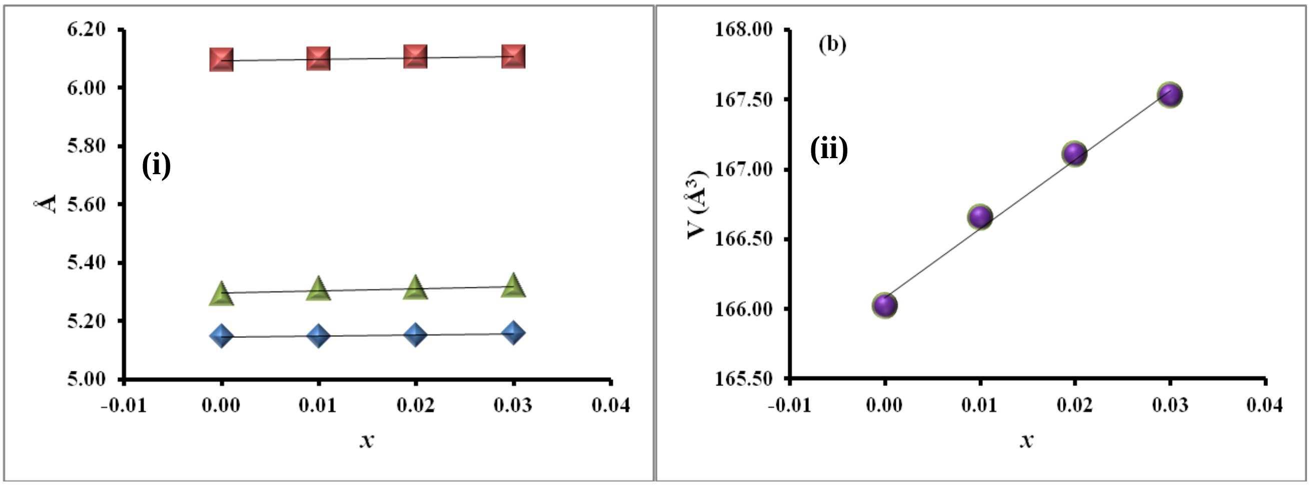

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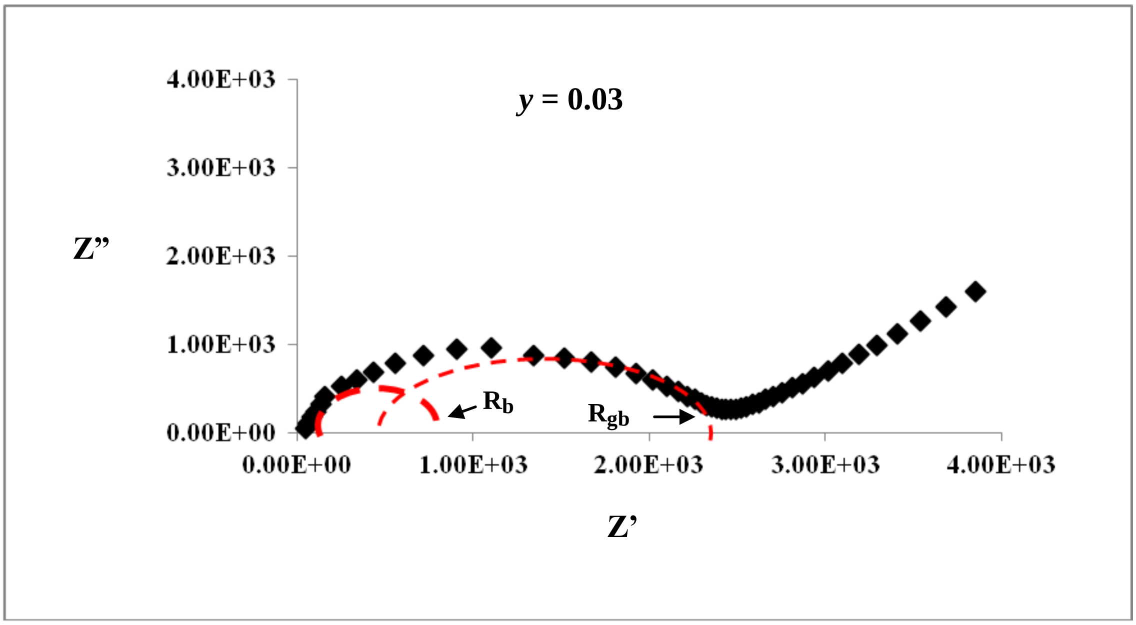
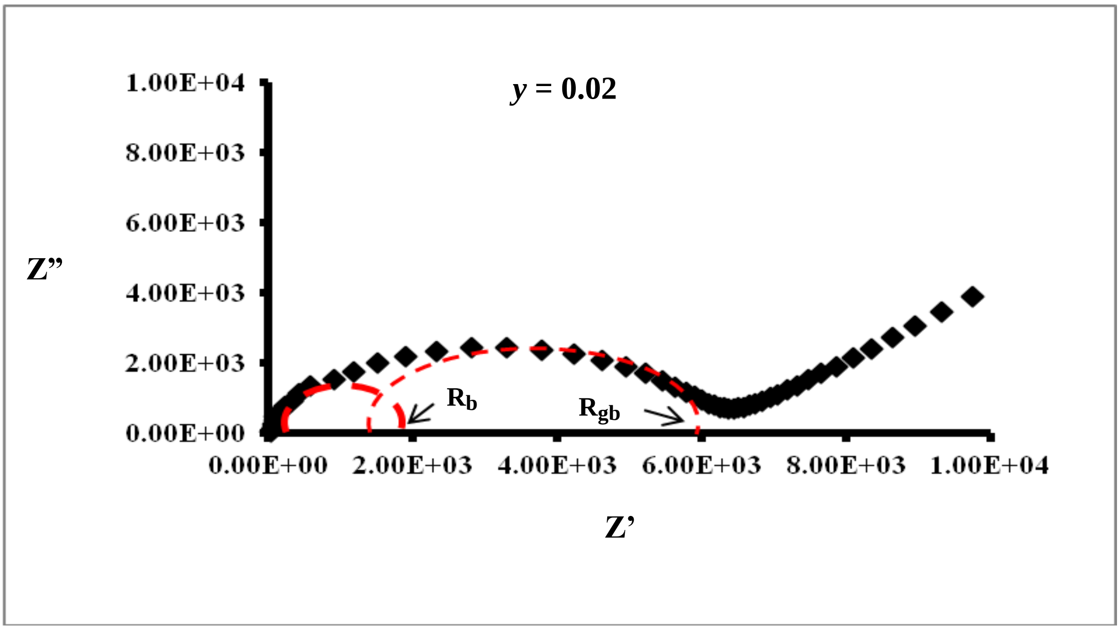
Figure 3. (i) Unit cell parameters and (ii) unit cell volume of $Li_{4.08+y}Zn_{0.04}Cr_ySi_{0.96-y}O_4$ samples

Meanwhile, the partial substitution also cause an increase of unit cell parameters and unit cell volume (Figure 3) in the structure. This is supposed to facilitate Li^+ mobility in the samples due to enlarge of migration channel and lowers the energy barriers which able to increase the ion hoping between the grain boundaries.

3.2 Direct current conductivity

Typical complex impedance for $Li_{4.08+y}Zn_{0.04}Cr_ySi_{0.96-y}O_4$ ($0.01 \leq y \leq 0.03$) compounds at 473 K are shown in Fig.4.





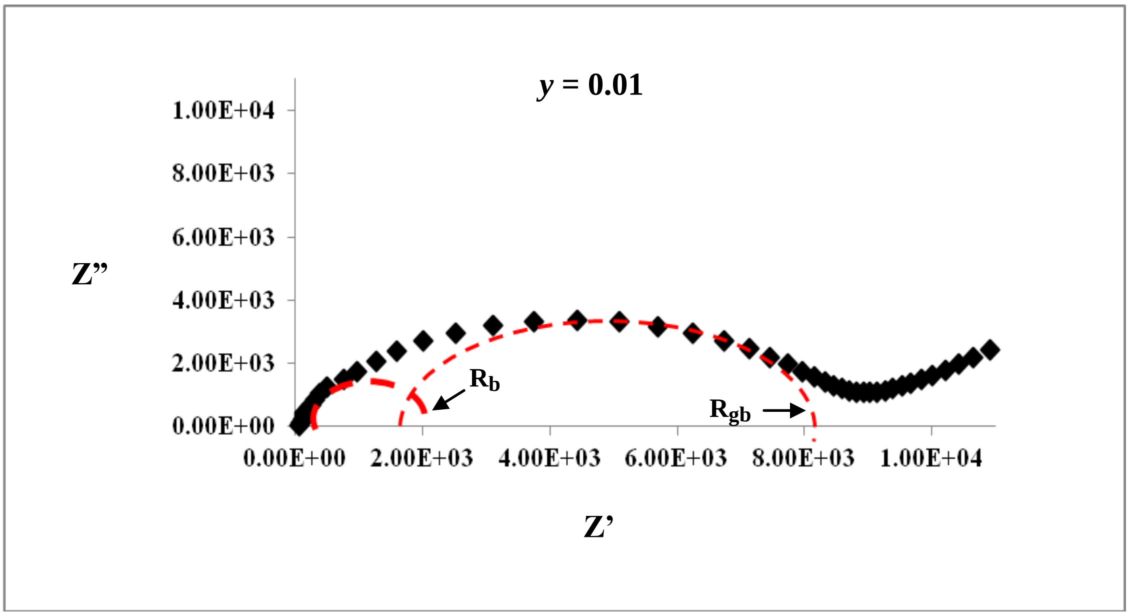


Figure 4. Typical complex impedance for $Li_{4.08+y}Zn_{0.04}Cr_ySi_{0.96-y}O_4$ ($0.01 \leq y \leq 0.03$) compounds

The total conductivity, (σ_t) (bulk conductivity, σ_b + grain boundary conductivity, σ_{gb}) which represent the direct current (d.c) conductivity in the ceramic sample can be calculated from equation [2] :

$$\frac{1}{\sigma_t} = \frac{1}{\sigma_b} + \frac{1}{\sigma_{gb}} \qquad (2)$$

where $\sigma_b = \frac{d}{AR_b}$ and $\sigma_{gb} = \frac{d}{AR_{gb}}$. In these equation, d is sample thickness, A is cross-sectional area of the sample, R_b is bulk resistance and R_{gb} is grain boundary resistance. As the substitution of y value (Cr^{3+}) increase, the total resistance, $R_t = (R_b + R_{gb})$ value shifts towards a lower value indicating increase in conductivity. The σ_b, σ_{gb} and σ_t of $Li_{4.08+y}Zn_{0.04}Cr_ySi_{0.96-y}O_4$ ($0.01 \leq y \leq 0.03$) compounds are listed in Table 1.

Table 1. The σ_b, σ_{gb} and σ_t of $Li_{4.08+y}Zn_{0.04}Cr_ySi_{0.96-y}O_4$ ($0.01 \leq y \leq 0.03$) compounds at 473 K

Compounds	σ_b (S cm^{-1})	σ_{gb} (S cm^{-1})	σ_t (S cm^{-1})
$y = 0.01$	6.84×10^{-5}	2.51×10^{-4}	1.80×10^{-5}
$y = 0.02$	7.53×10^{-5}	3.76×10^{-5}	2.51×10^{-5}
$y = 0.03$	1.88×10^{-4}	9.42×10^{-5}	6.27×10^{-5}

The arcs observed in the graphs can be represented by the equivalent circuit using combination of resistor, R_p and capacitor, C_p with constant phase element (CPE) behavior (Figure 5). The general expression of the CPE is [10] ;

$$Z = \frac{1}{C(j\omega)^n} \qquad (3)$$

Here, C indicates ideal capacitance where $n = 1$, $j = (-1)^{1/2}$ and ω shows the angular frequency.

The equivalent circuit consists of a series of array of parallel *RC* elements attached with a series resistor, R_s. Series resistance corresponds to bulk resistance whereas grain boundary resistance is represented by a resistance which is attached in parallel to a capacitor.

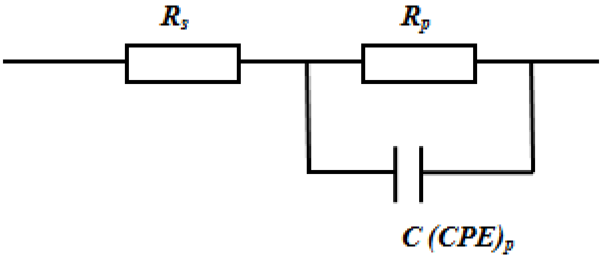


Figure 5. Equivalent circuit of the samples on the basis of impedance analysis

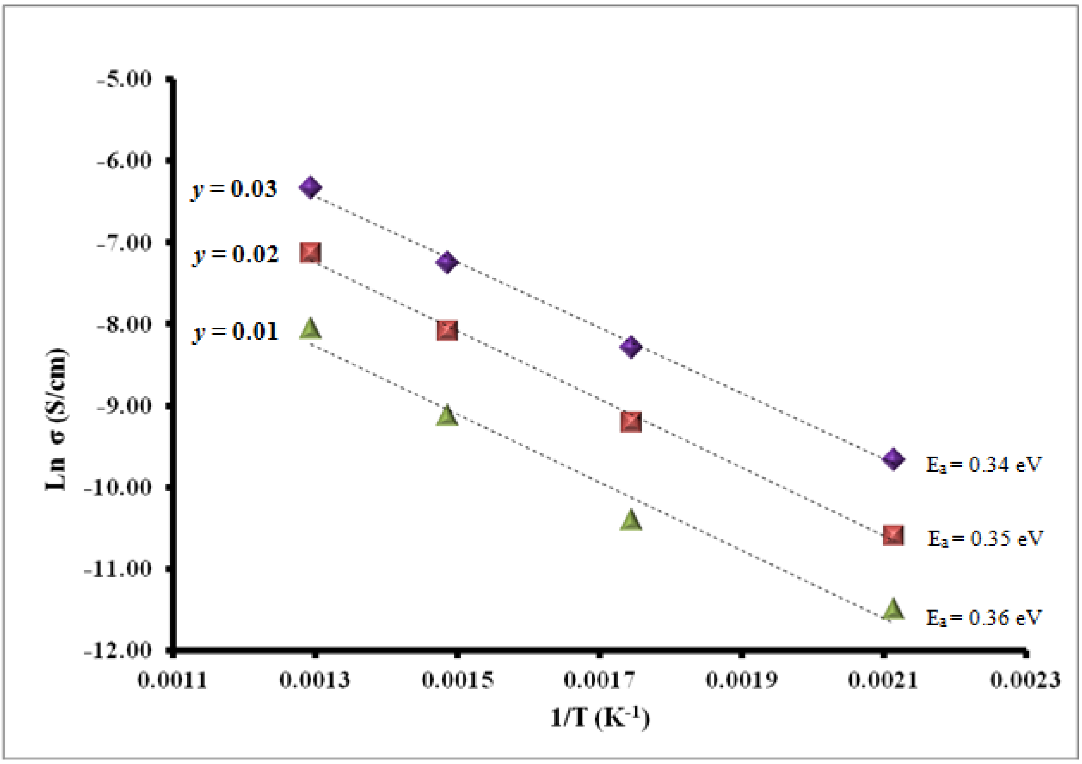


Figure 6. Temperature dependence of total conductivity for $Li_{4.08+y}Zn_{0.04}Cr_ySi_{0.96-y}O_4$ samples

Figure 6 presents the relationship between total conductivity of $Li_{4.08+y}Zn_{0.04}Cr_ySi_{0.96-y}O_4$ ($0.01 \leq y \leq 0.03$) with temperature. The total conductivities fit the Arrhenius equation:

$$\sigma_t T = A(T)\exp\left(\frac{-E_\alpha}{kT}\right) \tag{4}$$

where A is the pre-exponential factor, E_α is the activation energy for conduction and k is the Boltzman. The $Li_{4.08+y}Zn_{0.04}Cr_ySi_{0.96-y}O_4$ with $y = 0.03$ shows the highest total conductivity of 6.27×10^{-5} S cm^{-1} at 473 K and 2.44×10^{-3} S cm^{-1} at 773K. This value is an order of magnitude higher compared to the parent compound reported earlier by the authors [9]. The linear relationships are observed for the whole testing temperature range suggesting that there are no structure and phase changes in the samples. The activation energy of the samples was extracted from the slope of the Arrhenius graph and also shown in Figure 6. The low activation energy indicate an easier movement of lithium ion from one site to another in the lattice structure which resulting high mobility of ions and conductivity as well.

3.3 Alternating current conductivity

Fig. 7 depicts the frequency dependence conductivity spectra of $Li_{4.08+y}Zn_{0.04}Cr_ySi_{0.96-y}O_4$ ($0.01 \leq y \leq 0.03$) at 773 K. The conductivity spectra behavior obeys the universal power law : $\sigma_{Ac}(\omega) = \sigma(0) + A\omega^{\alpha}$ where σ(0) is the DC conductivity of the sample, A is a temperature dependant parameter and α is the power law exponent.

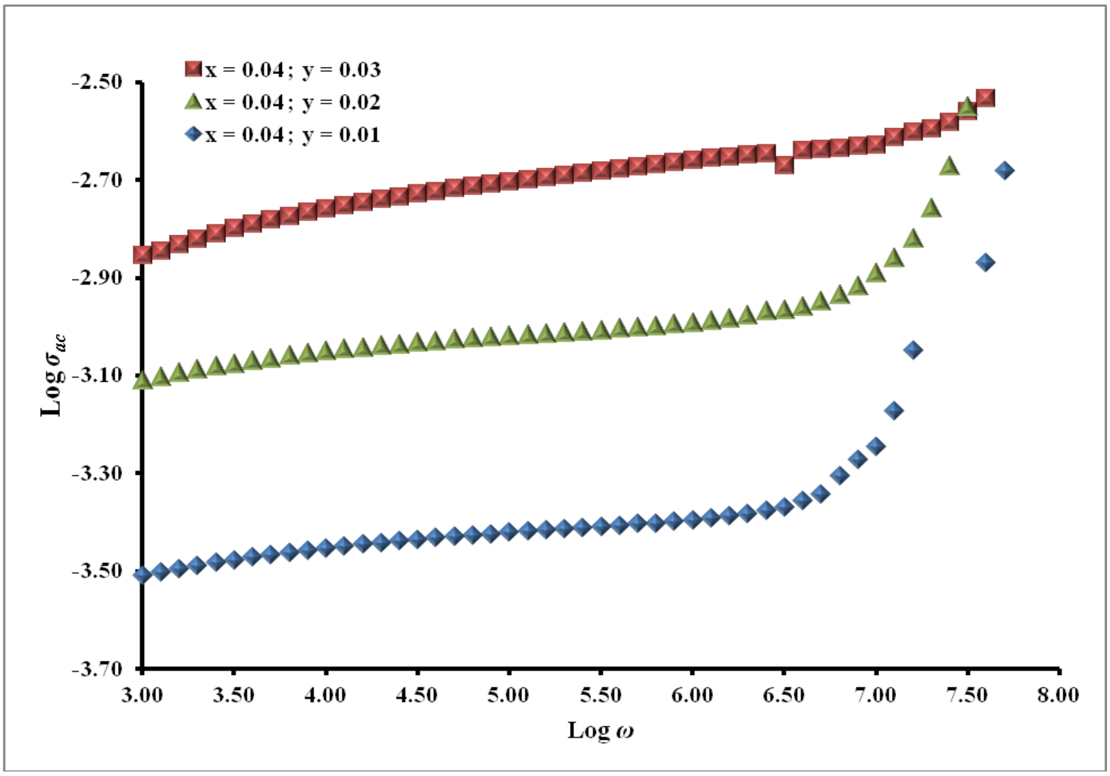


Figure 7. Conductivity spectra of $Li_{4.08+y}Zn_{0.04}Cr_ySi_{0.96-y}$ samples at 773 K

The ionic hopping, ω_p can be directly obtained from conductivity spectra data since it corresponds to $\sigma(\omega) = 2\sigma(0)$ [4,8,10-13]. Meanwhile the Li$^+$ concentration, C can be obtained using the equation [4,8,10-13]:

$$C = \frac{\sigma_t T}{\omega_p} = C = ne^2 a^2 \gamma k^{-1} \qquad (5)$$

where e is the electron charge, γ is the correlation factor which is set equal to 1, a is the jump distance between two adjacent sites for the ions to hope which is assumed to be 3Å for all materials, n is the concentration of mobile ions which can be calculated using Eq.5 and k is the Boltzmann constant. The Li$^+$ mobility, μ can be calculated using equation: $\mu = \sigma_t / ne$. The values of σ, ω_p, C and μ for the studied samples are tabulated in Table 2. The table shows that Li$^+$ concentration and mobility in the samples increase with increase of Cr^{3+}. This shows that inclusion of Cr^{3+} not only facilitates mobility of Li$^+$ ions but also increases the number of ions that contribute to conductivity enhancement.

Table 2. Parameters of σ, ω_p, C and μ for $Li_{4.08+y}Zn_{0.04}Cr_ySi_{0.96-y}O_4$ at 773 K

Compounds	σ (S cm^{-1})	ω_p (kHz)	K (S cm^{-1} K Hz^{-1})	μ (cm^2 V^{-1} s^{-1})
$y = 0.01$	3.16×10^{-4}	12.58	1.94×10^{-8}	1.70×10^{-11}
$y = 0.02$	7.96×10^{-4}	19.95	3.08×10^{-8}	2.70×10^{-11}
$y = 0.03$	2.44×10^{-3}	79.43	3.37×10^{-8}	1.07×10^{-10}

4. CONCLUSIONS

The effect of extra interstitial ions due to Cr^{3+} substitutions on the $Li_{4.08+y}Zn_{0.04}Cr_ySi_{0.96-y}O_4$ ($0.01 \leq y \leq 0.03$) compounds was investigated by X-ray diffraction and impedance spectroscopy. The XRD result indicated that Zn^{2+} and Cr^{3+} were successfully inserted into the Li_4SiO_4 structure. The compound showed enhanced conductivity (an order of magnitude higher than that of the parent compound) due to the presence of extra interstitial Li$^+$ ions that contributed to conductivity and their enhanced mobility.

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