JOURNAL OF MATERIALS SCIENCE **39** (2004) 727–729

Ion dynamic studies on $Li_3CaZr(PO_4)_3$

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The low equivalent weight and the high electropositive nature of Li^+ ions, which give high cell voltage and energy density for advanced electrochemical devices, have encouraged an intense search for a good Li^+ ion conductor. Recently lithium phosphate has attracted much attention because of its possible use in lithium electro chemical applications. In particular lithium compounds with NASICON structure have been studied extensively. One of the derivative materials of NASICON that has been extensively investigated is $CaZr_4(PO_4)_6$ which is isostructural with $NaZr_2P_3O_{12}$. $CaZr_4(PO_4)_6$ has high temperature thermal stability and excellent thermal shock resistance which makes it useful for battery applications. However the sinterability of this material is low compared with that of $NaZr_2P_3O_{12}$ [2–5]. Recently Yoon *et al.* reported that the addition of Li_2CO_3 to this material as a sintering aid would reduce the sintering temperature [6]. There are no reports on the electrical conduction due to the Li^+ ion motion in this material. The search for an improved ionic conductor related with Li phosphates is just one example demonstrating the current importance of conductivity studies on these materials [7]. In the present work Li^+ ion dynamics in $Li_3CaZr(PO_4)_3$ has been reported using electrochemical impedance spectroscopy.

The sample was prepared by solid-state reaction method. ZrO_2 was prepared by co-precipitation method. The raw material $ZrOCl_2{\cdot}8H_2O$ (>99% purity) was dissolved in distilled water and stirred well. Precipitation of the sample was carried out using NaOH as the hydrolyzing agent. The precipitate was washed thoroughly with water and dried in an oven at 120 °C for 5 h. The resultant agglomerates were ground into a fine powder using a mortar and pestle. The fine powder was calcined at 600 °C. For the preparation of $Li_3CaZr(PO_4)_3$ appropriate amounts of Li_2CO_3 (99.9%), $CaCO_3$ (>99.9%) ZrO_2 & $(NH_4)_2HPO_4$ (>99.9%) were mixed in an agate and mortar. The sample was then heated in a porcelain crucible at a temperature of 1000 °C. The resultant sample was ground into a fine powder and placed in a die. A pressure of around 4000 kg/cm^2 was been applied to form the pellet with a thickness of 0.1 cm and a diameter of 1 cm. The electrical conductivity and dielectric studies were carried out by using computer controlled HIOKI model 3532 LCR meter (frequency range 42 Hz–5 MHz) in the temperature range of 573–723 K with silver as an electrode.

Electrical characterization of ionic conductors has been carried out using the complex impedance (Z) plots. The advantages of using complex impedance for the analysis of ac response of solid electrolytes has been discussed by Hodge *et al.* [8]. Fig. 1 shows the complex impedance plot for $Li_3CaZr(PO_4)_3$. The data fall on a single semicircle whose center lies below the real axis. These high frequency semicircles are due to parallel combination of bulk resistance (R_b) and bulk capacitance (C_b) of the $Li_3CaZr(PO_4)_3$. The associated capacitance values were calculated at the maximum frequency using the relation $2\pi f_{max}RC = 1$. The observed semicircle has a capacitance of the order of pF and it is attributed to a conduction process through the bulk of the material [9].

Bulk resistance values were obtained from the low frequency intercept of the semicircle on the real, Z' axis using the program EQ developed by Boukamp [10, 11]. The bulk resistance value was found to be in the order of $10^7\ \Omega\,cm^{-1}$. The temperature dependence of bulk conductivity is shown in Fig. 2 and it is found to obey the Arrhenius equation given by

$$\sigma = \sigma_0 \exp^{-(E_a/KT)} \qquad (1)$$

where σ_0 is the pre-exponential factor, E_a is the activation energy. The activation energy for the sample is found to be 0.42 eV.

A plot of imaginary component of impedance as a function of frequency at different temperatures is shown in Fig. 3. The imaginary component of impedance (Z'') showed peak maxima at different temperatures. These peak maxima were shifted to low values of Z'' with rise in temperature and also shifts towards high frequency as in all solid electrolytes [12]. Also it is apparent from Fig. 3 that irrespective of the measured temperatures all the curves at high frequencies were merging with one another. This may be due the diminishing of the space charge effects at higher frequencies. The decrease in peak maxima at high temperatures may be due to increase in capacitance, which is attributed to the accumulation of charges at the electrode electrolyte interface [13]. At high temperatures the ions may be thermally activated resulting in the accumulation of charge carriers especially ions at the electrode/electrolyte interface.

The frequency dependence of the real part of the conductivity (σ'), at different temperatures is shown in Fig. 4. The curve displays a low frequency plateau,

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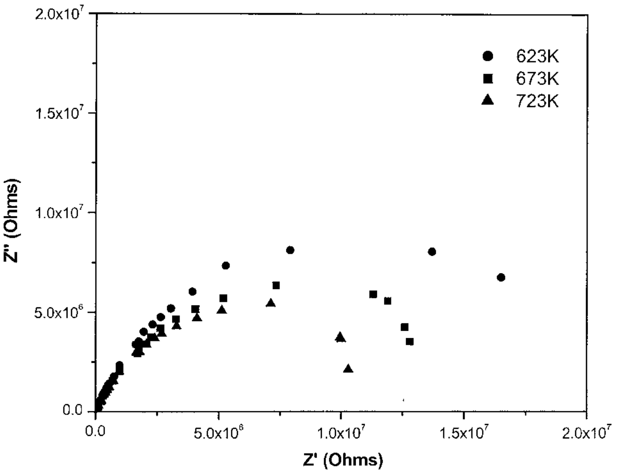

Figure 1 Complex impedance spectra for $Li_3CaZr(PO_4)_3$.

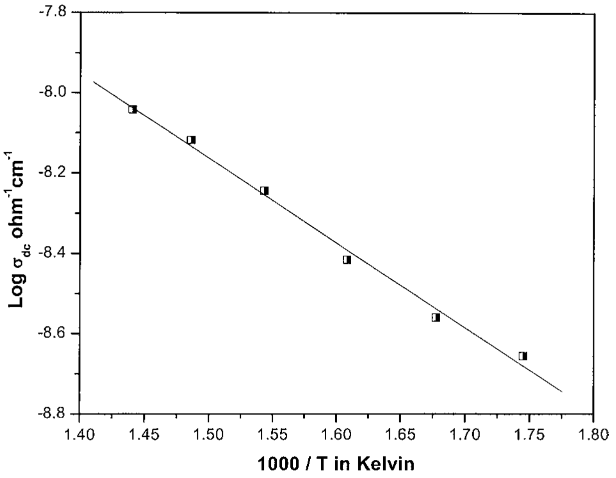

Figure 2 Arrhenius plot for $Li_3CaZr(PO_4)_3$.

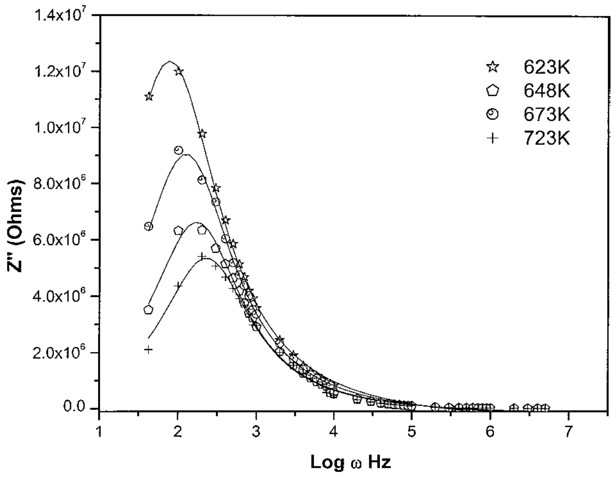

Figure 3 Variation of imaginary component of impedance as a function of frequency at different temperatures.

which corresponds to the *dc* conductivity of the material, and a dispersive region at high frequency. The existence of such a dispersive regime in the conductivity rules out the possibility that mobile ions perform a random hopping and reveals that the ionic motion is somehow correlated. The ac conductivity $\sigma(\omega)$, obeys the Jonscher's power law [14], and it is found to vary

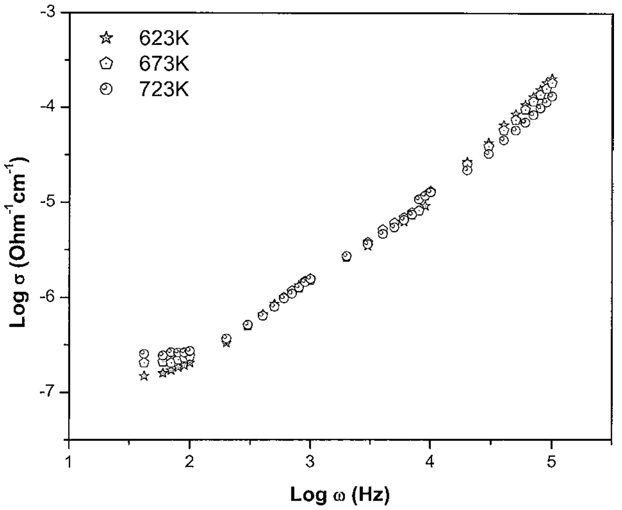

Figure 4 Conductivity spectra at various temperatures.

with angular frequency ω,

$$\sigma(\omega) = \sigma_{\mathrm{dc}} + A\omega^{\mathrm{n}} \tag{2}$$

where, σ_{dc} is the *dc* conductivity, A and n are temperature dependant parameters. Funke explained that the value of n might have a physical meaning [15]. According to this author, a value of n smaller than 1 would mean that the hopping motion involved is a translational motion with a big hop. On the other hand, value of "n" greater than 1 would mean that the motion involved is a localized hopping of the species with a small hop without leaving the neighborhood. In $Li_3CaZr(PO_4)_3$ the "n" value is found to be less than one at high temperatures (>350 °C). This suggests that the ion motion involved is a translational motion with a big hop. The hopping frequency has been extracted from the Almond and West formalism [16]

$$\omega_{\mathrm{H}} = (\sigma_{\mathrm{dc}}/A)^{1/\mathrm{n}} \tag{3}$$

The hopping frequency ω_{H} has been calculated from the conductivity spectra for all the samples at different temperatures. The *dc* conductivity estimated from the conductivity spectra are found to be in the order of 10^{-7} Ω^{-1} cm^{-1} at 723 K.

The dc conductivity of ionic conductors can be represented as [17],

$$\sigma_{\mathrm{dc}} = (Ne^2d^2\gamma/6)(\omega_{\mathrm{H}}/kT) \tag{4}$$

where N and e are the carrier concentration and charge, d and ω_{H} are the characteristic hopping distance and frequency and γ is a geometrical factor. In the case of isotropic materials the value of the geometrical factor and the hopping distance can be taken as 1/6 and 3 Å respectively [18]. The charge carrier concentration (N) has been calculated for the samples using the above values by substituting in Equation 4. The charge carrier concentration was found to be of the order of 10^{27} throughout the temperature range studied. The low conductivity of the sample even though it has high charge carrier concentration (10^{27} cm^{-3}), is due to the coulombic repulsive forces between the mobile charge carriers, which leads to the reduction of the velocity of the charge carriers and hence conductivity. This fact has also been confirmed from the broad nature of the modulus peak (not shown here). The width of the modulus peak becomes wider as the coulombic repulsive force between charge carriers become more extended [19].

The dielectric properties of any system may be characterized by frequency dependant parameters, which may define the complex permittivity. ε' and ε'' are calculated using the impedance data by the following equation

$$\varepsilon^* = 1/(j\omega C Z^*) \tag{5}$$

where Z^* is complex impedance, $C = (\varepsilon_0 A)/t$, t is thickness of the sample A is effective area of the electrodes, ε_0 is the vacuum permittivity (8.854×10^{-12} *F/m*), $\omega = 2\pi\nu$ and $j = \sqrt{-1}$. A plot of ε'' and log ω for $Li_3CaZr(PO_4)_3$ at different temperatures is presented in Fig. 5. The dispersion of dielectric constant is high at low frequencies at all temperatures. This behavior is attributed to the formation of space charge region at the electrode/electrolyte interface which is familiarly known as $\omega^{(n-1)}$ variation or the non-Debye type of behavior, where the space charge regions with respect to the frequency is explained in terms of ion diffusion [20]. At high frequencies due to high periodic reversal of the field at the interface, the contribution of charge carriers especially ions towards the dielectric constant decreases with increasing frequency.

In conclusion, $Li_3CaZr(PO_4)_3$ has been prepared by a solid state reaction method. A study of the lithium ion dynamics in $Li_3CaZr(PO_4)_3$ has been made using impedance spectroscopy. The impedance spectra yield a bulk conductivity as $10^{-7}\ \Omega^{-1}\,\text{cm}^{-1}$ and an activation energy as 0.42 eV. The presence of coulombic repulsive force between the charge carriers which leads to the low conductivity value has been confirmed by the conductance spectra. The dielectric spectra shows a low-frequency dispersion of the dielectric constant, which reveals the space charge effects arising from the electrode.

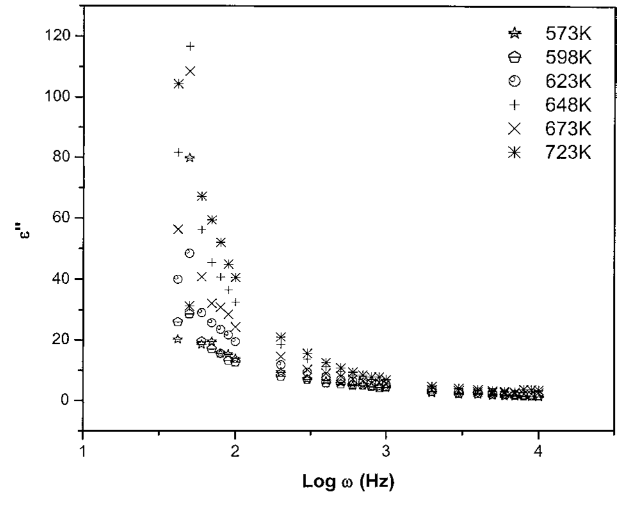

Figure 5 Dielectric spectra for $Li_3CaZr(PO_4)_3$.

Acknowledgments

Authors wish to thank Prof. B. A. Boukamp and Prof. Issac Abrahams for providing software for impedance data analysis.

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Received 15 May
and accepted 21 August 2003