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Ionic conductivity of Li_4SiO_4 solid solutions in the system $Li_2O–Al_2O_3–SiO_2$

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In the system $Li_2O–Al_2O_3–SiO_2$, Li_4SiO_4 forms two limited ranges of solid solutions: $Li_{4+x}Si_{1-x}Al_xO_4$: $0 < x \lesssim 0.4$, containing interstitial Li^+ ions and $Li_{4-3y}Al_ySiO_4$: $0 \leqslant y \lesssim 0.06$, containing Li^+ vacancies. The a.c. conductivity of polycrystalline samples of several compositions was measured over a range of frequency (2×10^2 to 5×10^4 Hz) and temperature (25 to 500° C). Both solid solutions, especially the Li^+ interstitial ones, have markedly higher conductivity than has stoichiometric Li_4SiO_4. This is due to an increase in the number of mobile ions and a decrease in the activation energy for conduction in the solid solutions.

1. Introduction

In the search for new Li^+ ion conducting solids with potential applications as solid electrolytes in batteries and solid-state devices, considerable interest has been shown in systems based on Li_4SiO_4 [1–16]. Li_4SiO_4 is a versatile host structure for solid solution formation. It forms limited ranges of solid solutions in the systems $Li_4SiO_4–Li_3YO_4$: Y = P, As and V, in which the conductivity of intermediate compositions is dramatically higher than that of either end-member. It also forms partial solid solutions with a variety of other oxides including Li_5AlO_4 [4], Li_2SO_4 [4], Li_2MoO_4 and Li_2ZnSiO_4 [1, 9]; these solid solutions also usually have enhanced conductivity.

The structure and polymorphism of Li_4SiO_4 is complex. By differential thermal analysis (DTA), a complex sequence of phase changes is observed in the range ~600 to 750° C [9]. Two polymorphs have been obtained at room temperature [10, 11]. Both are monoclinic but one is a weak superstructure of the other. The occurrence of ordered and disordered polymorphs may be related to the DTA effects at 600 to 750° C, and it has been suggested that a high temperature order–disorder transition is necessary in order to explain the temperature dependence of the conductivity of Li_4SiO_4 [7]. The crystal structures of the ordered and disordered polymorphs of Li_4SiO_4 are built of isolated SiO_4^{4-} tetrahedra, linked together by Li^+ ions which occupy a variety of sites of coordination number 4, 5 and 6 [10, 11]. The packing arrangement of the oxide ions in Li_4SiO_4 is intermediate between hexagonal close packed and the recently discovered, tetragonal packed [12, 13].

Of the various solid solution systems, that of $Li_4SiO_4–Li_3PO_4$ has been most studied [3–6, 14–16]. The phase diagram has been determined [6], the conductivity measured as a function of composition and temperature [3–6], ^7Li nuclear magnetic resonance (NMR) measurements made [14], the crystal structure of one solid solution composition, $Li_{3.75}(Si_{0.75}P_{0.25})O_4$, determined [15], and a lithium/iodine cell constructed using $Li_{3.4}(Si_{0.4}P_{0.6})O_4$ as the solid electrolyte [16].

2. Experimental details

Polycrystalline samples of Li_4SiO_4 were prepared using standard procedures; the reagents were Li_2CO_3 (Analar) and SiO_2 (high purity quartz sand) which were mixed and reacted in gold foil boats, in air, at 800 to 900° C. The product was crushed finely and completeness of reaction was checked by X-ray powder diffraction using a Philips Hägg Guinier camera, with $CuK\alpha_1$ radiation. Similar methods were used to prepare the solid solutions: high purity Cera alumina was used as the source of Al_2O_3.

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Pellets for conductivity measurements were cold-pressed at ~ 50 000 psi* and reheated at 800 to 900° C for a few hours in order to increase their mechanical strength. Typically, pellets had a porosity of 20 to 30%. Gold foil electrodes were attached to the pellet faces using gold paste (Hanovia liquid gold 8177, Englehard), the paste was decomposed and hardened by gradually heating to 500° C, and the pellet loaded into a two terminal conductivity cell. The cell constant, k, was determined from the area of the electrodes and the pellet thickness. Although k had an uncertainty of ~ 25%, this was tolerable compared with the large variations of conductivity with temperature and composition. A chromel/alumel thermocouple was placed close to the pellet and the cell placed inside a vertical tube furnace whose temperature was controlled and measured to ± 3° C. The furnace and cell were allowed to equilibrate prior to conductivity measurements. The conductivity was measured with a Wayne Kerr B224 admittance bridge over the frequency range 500 Hz to 50 kHz using a Brookdeal 9473 signal source and a Philips PM 3232 oscilloscope as a detector.

3. Results

3.1. Synthesis of Li_4SiO_4 solid solutions

A variety of compositions in the lithia-rich corner of the system Li_2O–Al_2O_3–SiO_2 were prepared and reacted in order to look for the occurrence of solid solutions based on Li_4SiO_4, as well as any possible new phases. A most unusual result was that Li_4SiO_4 forms *two* separate partial solid solution series on the joins with $LiAlSiO_4$ and Li_5AlO_4, respectively, as shown in Fig. 1. On the join Li_4SiO_4–Li_5AlO_4, the replacement mechanism is

$$Si^{4+} \rightleftharpoons Al^{3+} + Li^+$$

Hence, Al^{3+} ions occupy Si^{4+} sites and the extra Li^+ ions must occupy interstitial sites. The solid solution formula may be written:

$$Li_{4+x}Si_{1-x}Al_xO_4\colon\ 0 < x \lesssim 0.4$$

On the join Li_4SiO_4–$LiAlSiO_4$, the replacement mechanism is

$$3Li^+ \rightleftharpoons Al^{3+}$$

Hence, Al^{3+} ions occupy Li^+ sites and additional Li^+ vacancies are created giving an overall formula:

$$Li_{4-3y}Al_ySiO_4\colon\ 0 < y \lesssim 0.6.$$

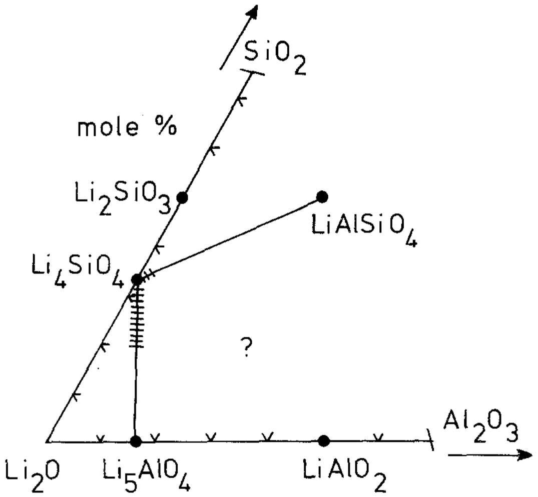

Figure 1 Li_4SiO_4 solid solutions in the system, Li_2O–Al_2O_3–SiO_2.

There was no evidence for the formation of Li_4SiO_4 solid solutions on the join Li_4SiO_4–$LiAlO_2$ although the X-ray powder patterns of reacted mixtures indicated the existence of new phases in this region of the diagram; no further attempts have been made to characterize these phases.

3.2. Conductivity of Li_4SiO_4 solid solutions

Typical a.c. conductivity data for one composition, $Li_{3.82}Al_{0.06}SiO_4$ (vacancy solid solution), are shown in Fig. 2 as log conductivity (σ) against log frequency (f). At high temperatures and conductivities, a frequency independent conductivity is observed over the entire frequency range but at lower temperatures, the conductivity plateau appears at lower frequencies only. These frequency independent conductivites were taken as the effective bulk, d.c. conductivities. The dispersion observed at low temperatures and high frequencies is attributed to bulk relaxations or migration losses. In this region, the a.c. conductivity data fit the Jonscher equation, $\sigma_{ac} = \sigma_{dc} + A\omega^n$ [17], where A and n are constants and ω is the angular frequency, $2\pi f$.

Some data sets were replotted in the complex admittance plane, Y'' ($k\omega Cp$) against $Y'(\sigma)$, where Cp is the experimental bridge capacitance reading, as shown in Fig. 3. The data fall on spikes which are inclined to the vertical. There is no sign of any high frequency semicircle in the plots and hence the intercepts of the spikes on the real (Y') axis

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*1 psi = 6.89 × 10^3 Pa.

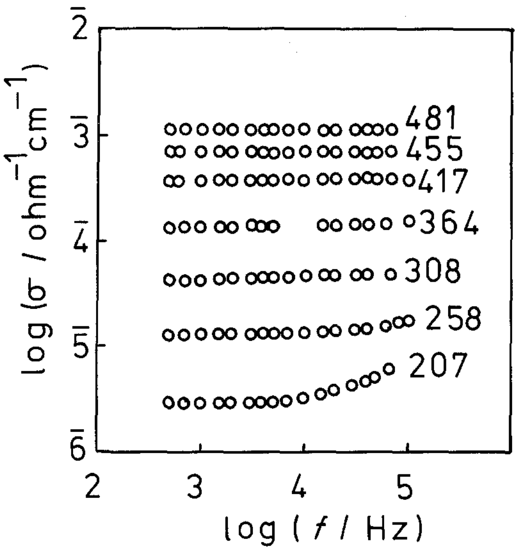

Figure 2 Conductivity against frequency for different temperatures (° C) of the pellet $Li_{3.82}Al_{0.06}SiO_4$.

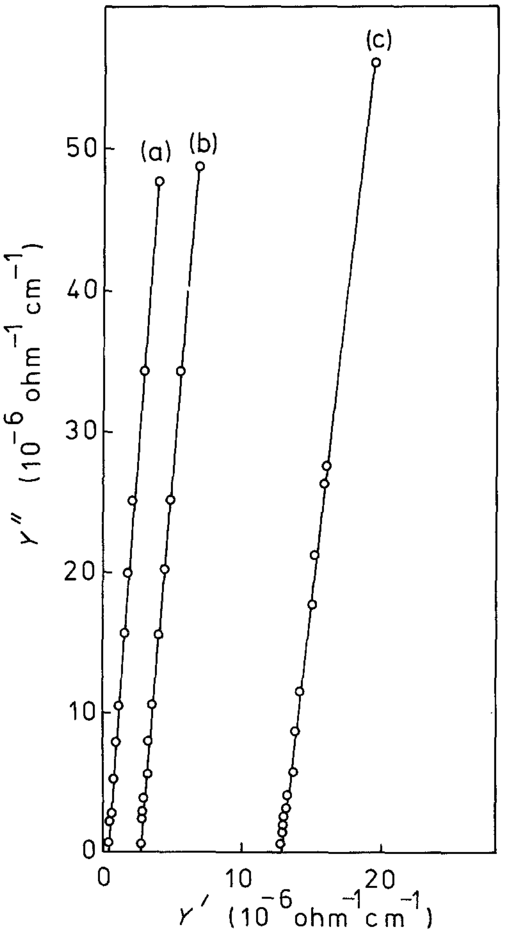

Figure 3 Complex admittance plots for three different pellets: (a) Li_4SiO_4 at 206° C, (b) $Li_{3.82}Al_{0.06}SiO_4$ at 207° C, (c) $Li_{4.3}Al_{0.3}Si_{0.7}O_4$ at 104° C.

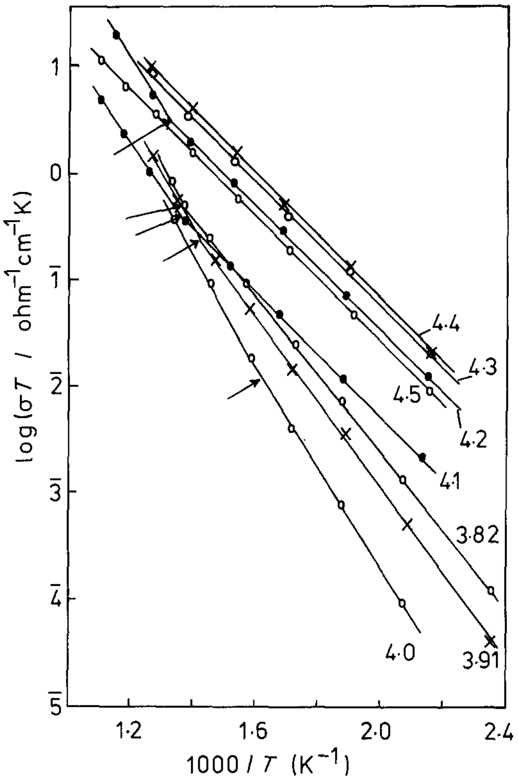

Figure 4 Arrhenius conductivity plots. Lithium content is marked on each.

represent the bulk crystal conductivites. Within experimental error, these values were the same as the frequency independent conductivities observed in plots such as Fig. 2. For most data sets therefore, the bulk conductivites were simply extracted from plots such as Fig. 2.

The bulk conductivities are shown in Arrhenius format as a function of temperature and composition in Fig. 4. Data for Li_4SiO_4 show a change in slope at ~300° C, as reported previously [2, 7]. A change in slope is also seen, arrowed, in the vacancy and several of the interstitial solid solutions, but the change occurs at higher temperatures in the solid solutions than in stoichiometric Li_4SiO_4.

The conductivity of both solid solution series, especially the interstitial solid solutions, is higher than that of Li_4SiO_4. This is further shown in Fig. 5 where conductivity is plotted against composition for two temperatures. In the interstitial solid solutions, the conductivity reaches a constant maximum value for compositions with $x \sim 0.25$ to 0.40.

Activation energies, E, and pre-exponential factors, A, were extracted from the Arrhenius plots

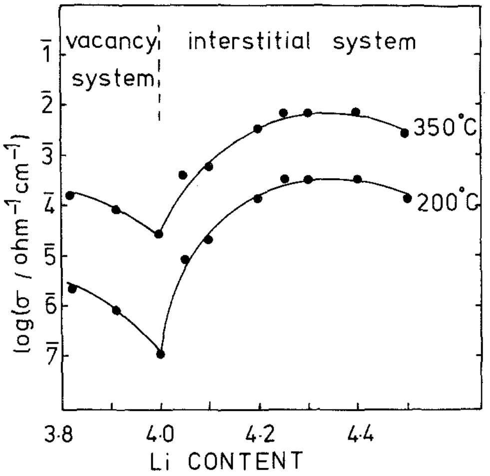

Figure 5 Conductivity against composition at two temperatures.

given in Fig. 4 and are plotted against composition in Fig. 6. For most compositions, two E and A values are given. These are for the high temperature, (HT) and low temperature (LT) conductivity data above and below the changes of slope seen in Fig. 4. For the lithium-rich, interstitial solid solutions ($x \gtrsim 0.2$) the HT and LT regions appear to merge in Fig. 6. Also shown in Fig. 6 is the variation in the temperature of the change-over from the LT to the HT region as a function of composition.

4. Discussion

Li_4SiO_4 is a versatile material for doping or solid solution formation; silicon can be replaced by other cations of the same or different charge and the lithium content can be either increased above or decreased below four. In the present solid solutions, it is possible to introduce either Li^+ ion vacancies or interstitial Li^+ ions into the structure of Li_4SiO_4 by the respective mechanisms:

$$3Li^+ \rightarrow Al^{3+} + 2\ \text{vacancies}$$

$$Si^{4+} \rightarrow Al^{3+} + Li^+\ \text{interstitial}$$

In both cases, but particularly in the latter, a large increase in conductivity occurs on solid solution formation.

Some insight into the mechanism of conduction in Li_4SiO_4 and the reasons for conductivity enhancement on solid solution formation, is obtained by analysing the conductivity data, Fig. 4, in terms of random walk theory using the equation:

$$\sigma T = A\ \exp(-E/kT) \qquad (1)$$

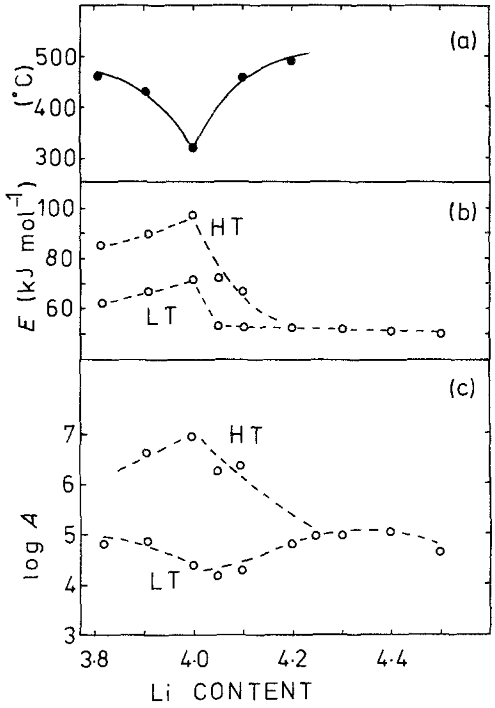

Figure 6 (a) Variation in LT–HT change-over temperature with composition. Variation of (b) activation energy and (c) pre-exponential factor with composition.

$$= N(ze)^2a^2k^{-1}\gamma c(1-c)\omega_0\exp(\Delta s/k)\exp(-E/kT) \qquad (2)$$

where N is the number of lattice sites for the mobile ions and c their fractional occupancy, (ze), a and ω_0 are the charge, jump distance and fundamental vibrational frequency of the mobile ions, γ is a geometrical factor which may also include a correlation factor (often $\frac{1}{2}$ or $\frac{1}{3}$), k is Boltzmann's constant, and ΔS and E are the entropy and activation energy for conduction.

Many of these parameters are not known accurately, but nevertheless, a semiquantitative analysis is possible if certain assumptions are made, i.e. that $a \sim 0.3$ to 0.5 nm, $\omega_0 \sim 1 \times 10^{13}$ Hz, $\gamma \sim \frac{1}{3}$ and that $Nc(1-c)$ may be lumped into a single term, c', representing the effective number of mobile ions. It has been shown that for Li_4SiO_4 in the LT region, $\exp(\Delta s/k)$ is approximately 50 [18]. This enables A to be partially evaluated leaving c' as the only unknown; c' may then be estimated by comparison with the experimental A values, Fig. 6.

Using Equation 2 and the values given above for the various component parameters, the conductivity data, Figs. 4 to 6, may be explained, as follows.

For pure Li_4SiO_4, the conductivity data show a change in slope at ~300° C. In the LT region, the carrier concentration is small, $\lesssim 1\%$ and independent of temperature [7, 18]. The activation energy represents the energy of migration of the Li^+ ions. In the HT region, the carrier concentration is thermally activated; the entropy of creation contributes to the value of A giving it an anomalously high value, $\gtrsim 10^7$; the energy of creation contributes to E, increasing its value by about 30 kJ mol^{-1} [7]. The behaviour of Li_4SiO_4 is therefore somewhat similar to the extrinsic–intrinsic behaviour observed with doped alkali halides but with the difference that it appears to be a property of pure Li_4SiO_4.

In the Li_4SiO_4 solid solutions, several effects may be seen. With increasing departure from Li_4SiO_4: the conductivity increases dramatically, especially in the interstitial solid solutions; the change-over from the LT to HT region occurs at progressively higher temperaures; the activation energy in both LT and HT regions decreases; the A value in the LT region increases, but in the HT region decreases. Most of these effects have a common origin which is that in the LT region, the carrier concentration, c', increases in both solid solution series. This is seen directly in the compositional dependence of A in the LT region: the value of A (and therefore c') in the solid solutions is about one order of magnitude larger than in Li_4SiO_4. Since c' is larger in the solid solutions, the change-over from the LT to HT region is displaced to higher temperature. As c' increases, so the distinction between the LT and HT regions decreases, and the two regions appear to be indistinguishable in the lithia-rich solid solutions for $x \gtrsim 0.2$.

The activation energy of migration, E, also decreases in the solid solutions but the reasons for this are not well understood. It could possibly be a size effect, if the sizes of the window, through which a moving ion must pass, increase in both solid solution series. Alternatively, it could be a consequence of co-operative processes in concentrated carrier systems: in β-alumina, calculations have shown that the activation energy for migration of Na^+ ions is greatly reduced by co-operative interactions between the mobile ions themselves [19]. Perhaps, in the present solid solutions, c' is large and co-operative interactions are also important.

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