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# $Li^+$ Ion Conductivity in the System $Li_4SiO_4$–$Li_3VO_4$

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Two ranges of solid solutions were prepared in the system $Li_4SiO_4$–$Li_3VO_4$: $Li_{4-x}Si_{1-x}V_xO_4$, $0 < x \leq 0.37$ with the $Li_4SiO_4$ structure and $Li_{3+y}V_{1-y}Si_yO_4$, $0.18 \leq y \leq 0.53$ with a $\gamma$ structure. The conductivity of both solid solutions is much higher than that of the end members and passes through a maximum at $\sim 40Li_4SiO_4 \cdot 60Li_3VO_4$ with values of $\sim 1 \times 10^{-5}$ ohm$^{-1}$ cm$^{-1}$ at 20°C, rising to $\sim 4 \times 10^{-2}$ ohm$^{-1}$ cm$^{-1}$ at 300°C. These conductivities are several times higher than in the corresponding $Li_4SiO_4$–$Li_3(P,As)O_4$ systems, especially at room temperature. The solid solutions are easy to prepare, are stable in air, and maintain their conductivity with time. The mechanism of conduction is discussed in terms of the random-walk equation for conductivity and the significance of the term $c(1 - c)$ in the preexponential factor is assessed. Data for the three systems $Li_4SiO_4$–$Li_3YO_4$ ($Y$ = P, As, V) are compared.

## Introduction

Several studies have been made of $Li^+$ ion conductivity in solid solutions based on (i) $Li_4XO_4$ ($X$ = Si, Ge), and (ii) $\gamma$ tetrahedral structures such as $Li_3PO_4$, $Li_3AsO_4$, and $Li_2ZnGeO_4$ (LISICON) (*1–13*). In all cases where solid solutions form, either by the creation of $Li^+$ vacancies or interstitials, the conductivity increases by several orders or magnitude, compared with the conductivity of the end members. Attempts have been made to use these solid electrolytes in cells. While LISICON, $Li_{14}ZnGe_4O_{16}$, exploded in contact with lithium metal (*14*), pellets made from $Li_4SiO_4$–$Li_3PO_4$ solid solutions have been used satisfactorily in a $Li/I_2$ cell (*15*).

The systems $Li_4SiO_4$–$Li_3YO_4$ ($Y$ = P, As), have been studied previously and showed considerable similarities (*3–5, 12, 13*). Maximum conductivities were found in compositions around $40 Li_4SiO_4 \cdot 60Li_3YO_4$, with values of $\sim 2 \times 10^{-6}$ ohm$^{-1}$ cm$^{-1}$ at 20°C rising to $\sim 2 \times 10^{-2}$ ohm$^{-1}$ cm$^{-1}$ at 300°C. The present study reports on the system $Li_4SiO_4$–$Li_3VO_4$, in which the maximum conductivities are several times higher than in the corresponding phosphate and arsenate systems.

The experimental details of sample preparation, analysis by X-ray diffraction and DTA, preparation of pellets, electrodes and conductivity measurements were as described previously (*13*). After the pellets were cold-pressed they were fired at 1000 to 1050°C for 18 to 24 hr to increase their mechanical strength and to reduce the importance of intergranular effects; final pellet porosities were 10 to 15%. The samples were white before and after sintering, indicating that no significant reduction of $V^{5+}$ had occurred.

## Results and Discussion

A partial phase diagram for the system $Li_4SiO_4$–$Li_3VO_4$ is shown in Fig. 1. This

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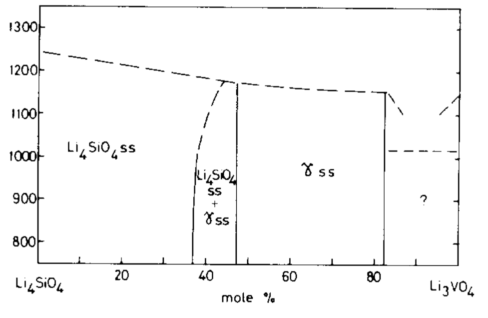

FIG. 1. Partial phase diagram for the system $Li_4SiO_4$–$Li_3VO_4$.

was constructed using the results of heating experiments on compositions with $Li_4SiO_4$/$Li_3VO_4$ ratios of 95/5, 90/10, 80/20, 65/35, 60/40, 40/60, 30/70, 20/80, 15/85, 10/90, and 5/95. The phase diagram shows an extensive range of $Li_4SiO_4$ solid solutions containing up to ~37% $Li_3VO_4$. There was some evidence that the solid solutions may extend a little further, perhaps up to 44% $Li_3VO_4$, at temperatures close to the solidus. An extensive range of γ solid solutions exists, from ~46 to 82% $Li_3VO_4$; these solid solution limits appear to be temperature independent. An unusual feature of the γ solid solutions is that they do not extend to 100% $Li_3VO_4$, which has a high temperature γ polymorph, stable above ~750°C (*16*). This contrasts with the systems $Li_4SiO_4$–$Li_3PO_4$ and $Li_4SiO_4$–$Li_3AsO_4$ which show an uninterrupted range of γ solid solutions from, e.g., 60 to 100% $Li_3(P,As)O_4$ (*12*, *13*). Melting temperatures across the diagram were determined approximately and are shown as the dashed curve; no attempt was made to determine separately the solidus and liquidus curves. The melting temperatures drop slightly over the range 0 to ~80% $Li_3VO_4$. In the range 85 to 95% $Li_3VO_4$, melting temperatures drop abruptly to ~1020°C. The crystalline phases which appear below 1020°C over the latter composition range have not been characterized. They do not correspond to any of the known polymorphs of $Li_3VO_4$ (*16*).

The variation of unit cell parameters of the $Li_4SiO_4$ and γ solid solutions with composition is shown in Fig. 2. Unit cell volumes are shown in Fig. 3 together with the volumes of the corresponding arsenate and phosphate solid solutions for comparison (*12*, *13*, *17*). The $Li_4SiO_4$ solid solution cell volumes are shown doubled since the unit cell of $Li_3(P, As)O_4$ contains four formula units whereas that of $Li_4SiO_4$ contains only two. It is noteworthy that, although the end-member phases, e.g., $Li_4SiO_4$ and $Li_3VO_4$, have quite different unit cell volumes, the volumes become increasingly similar in the solid solutions. The discontinuity in cell volume plots over the range 35 to 50% $Li_3VO_4$ in Fig. 3 is associated with the two-phase region of $Li_4SiO_4$ss + $Li_3VO_4$ss on the phase diagram (Fig. 1). The two solid solution phases present in this region in fact have quite similar cell volumes; although the *a*, *c* cell parameters (Fig. 2) are different in each, the effect of these differences is canceled in the volumes.

Conductivities were measured on cold-pressed pellets which had been sintered at

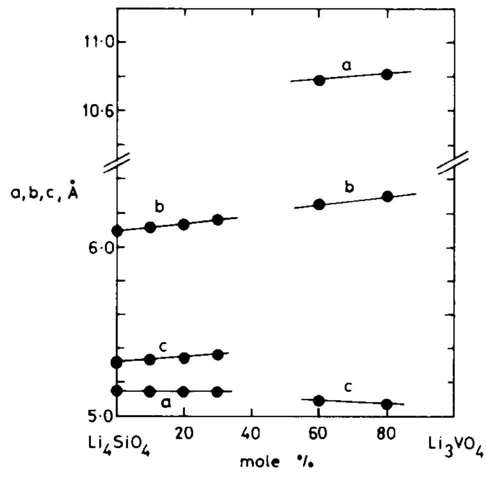

FIG. 2. Unit cell parameters of $Li_4SiO_4$–$Li_3VO_4$ solid solutions.

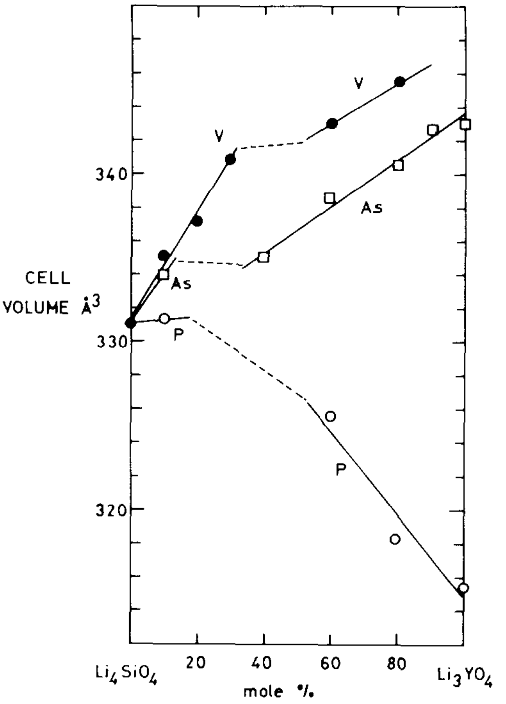

FIG. 3. Unit cell volumes of solid solutions in the systems $Li_4SiO_4$–$Li_3YO_4$ ($Y$ = P, As, V). The volumes of the silicate solid solutions are shown doubled in order to facilitate comparison.

1025 to 1050°C. The a.c. conductivity data were analyzed by plotting in the complex admittance plane and as spectroscopic plots of the complex impedance and complex electric modulus, as described previously (*13*). These analyses showed that significant grain boundary effects were not present. Thereafter, data were plotted as log conductivity vs log frequency and the bulk pellet conductivities were extracted from the values of the frequency independent conductivity plateaux. Individual plot points are not shown in Fig. 4 but were for 6 or 7 temperatures in the range ~25 to 350°C. The conductivities of the end members, especially $Li_3VO_4$, are very low but increase by many decades in the solid solutions and pass through a broad maximum at ~$40Li_4SiO_4 \cdot 60Li_3VO_4$. This composition, which has a $\gamma$ structure (Fig. 1) has a conductivity of ~$1 \times 10^{-5}$ ohm$^{-1}$ cm$^{-1}$ at 20°C rising to ~$4 \times 10^{-2}$ ohm$^{-1}$ cm$^{-1}$ at 300°C. Similar trends, with a conductivity maximum, were observed in the $Li_4SiO_4$–$Li_3(P,As)O_4$ systems but the maximum conductivity in these systems was lower, ~1 to $2 \times 10^{-6}$ ohm$^{-1}$ cm$^{-1}$ at 20°C (*12*, *13*). The conductivity of selected $Li_4SiO_4$–$Li_3VO_4$ pellets was remeasured after storing at room temperature for several months. No significant decrease in conductivity had occurred.

The conductivity data were replotted as log $\sigma T$ vs $T^{-1}$ (not shown). The plots were again linear, as were the log $\sigma$ vs $T^{-1}$ plots (Fig. 4) and hence it was not possible to decide, on these data alone, which method of presentation is preferable. The activation energy $E$ and preexponential factor $A$ were obtained from the slopes and intercepts of the log $\sigma T$ vs $T^{-1}$ plots and are plotted as a function of composition in Fig. 5. Data for compositions 85 to 100% $Li_3VO_4$ are excluded since these materials were only poorly conducting and did not have a $\gamma$

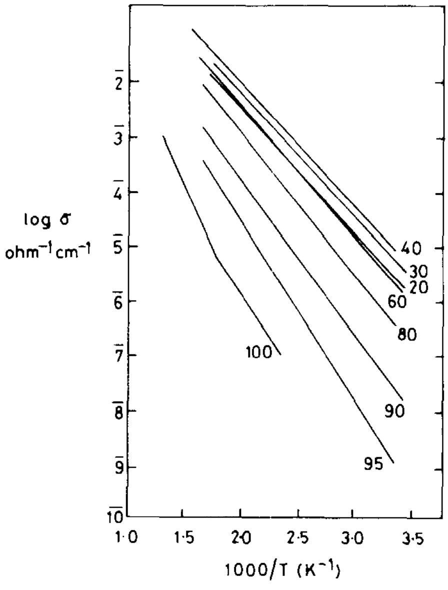

FIG. 4. Conductivity of $Li_4SiO_4$–$Li_3VO_4$ solid solutions. Numbers refer to $\%Li_4SiO_4$ content.

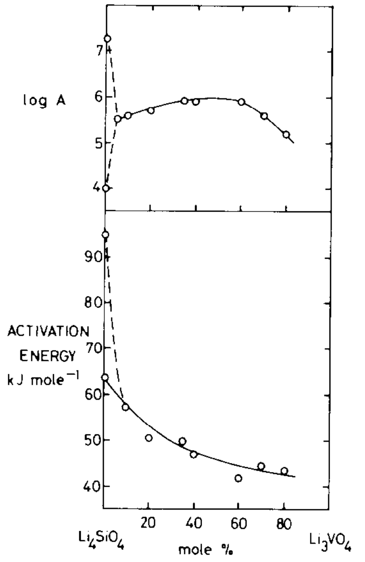

FIG. 5. Variation of conductivity preexponential factor and activation energy with composition.

structure. The data in Fig. 5 fall on smooth curves and do not show any discontinuity at the changeover from $Li_4SiO_4$ to $\gamma$ crystal structure type between 40 and 60% $Li_3VO_4$. This is consistent with the previous observation that the actual crystal structure, whether $Li_4SiO_4$ or $\gamma$ type, does not have a major influence on the magnitude of the conductivity in the system $Li_4SiO_4$–$Li_3PO_4$; of far greater importance is the total $Li^+$ content in the solid solutions (*12, 13*).

The general appearance of Fig. 5 is similar to that observed in the corresponding phosphate and arsenate system (*12, 13*). The activation energy decreases to $\sim 43 \pm 3$ kJ $mole^{-1}$ in the more highly conducting of the $Li_4SiO_4$ and $\gamma$ solid solutions. At the same time, the preexponential factor passes through a maximum value of $\sim 8 \times 10^5$. The explanation of these trends is as follows.

$Li_4SiO_4$ shows a change in slope of the Arrhenius conductivity plot at ~300°C. Below 300°C the low value of the preexponential factor (obtained by extrapolation) of $\sim 10^4$ is attributed to the small number of $Li^+$ ions that are mobile (*13*). This is consistent with the results obtained from a new method of analysis of a.c. conductivity data which, for $Li_4SiO_4$, indicated that over the temperature range 123 to 230°C, the number of mobile $Li^+$ ions is constant and equal to ~0.6% of the total $Li^+$ content (*18*). Above 300°C, the preexponential factor is anomalously high, $\gtrsim 10^7$. This is because the concentration of mobile $Li^+$ ions is temperature dependent in this region (*13*). The change in slope of the conductivity Arrhenius plot at 300°C therefore shows similarities to the extrinsic/intrinsic behavior of doped alkali halides but with the difference that it appears to be a property of pure $Li_4SiO_4$ (*2*). The activation energy below 300°C in $Li_4SiO_4$, ~64 kJ $mole^{-1}$, is associated with the migration of the mobile $Li^+$ ions. Above 300°C, the activation energy, ~94 kJ $mole^{-1}$, contains an additional contribution of ~30 kJ $mole^{-1}$ which is associated with the creation of mobile $Li^+$ ions.

On addition of $Li_3VO_4$, and $Li_3(P, As)O_4$, to $Li_4SiO_4$, several effects are observed: the change in slope of the Arrhenius conductivity plot moves to higher temperatures, the conductivity increases, the activation energy decreases and the preexponential factor adopts a value that is intermediate between the two values obtained for $Li_4SiO_4$. A partial explanation of these effects is that, by the time a few percent of $Li_3VO_4$ has been added, a significant portion, if not all, of the $Li^+$ ions are effectively mobile. This accounts qualitatively for an increase in the preexponential factor (at low temperatures) of between 1 and 2 orders of magnitude. It also means that the high temperature behavior, in which the concentration of mobile $Li^+$ ions is temperature dependent, can no longer be observed.

A facile explanation as to why the carrier concentration should be composition dependent, is that, in $Li_4SiO_4$, $Li^+$ vacancies are the predominant current carriers. The concentration of these is small in $Li_4SiO_4$, but increases greatly on forming solid solutions with $Li_3VO_4$, by means of the substitution mechanism, $Li^+ + Si^{4+} \rightarrow V^{5+}$. In a similar manner, the increase in carrier concentration and conductivity of $Li_3$(P, As, V)$O_4$, on forming solid solutions with $Li_4SiO_4$, can be explained: it is assumed that interstitial $Li^+$ ions are the mobile species and the concentration of these in stoichiometric $Li_3$(P, As, V)$O_4$ is small. On forming solid solutions with $Li_4SiO_4$, the concentration of interstitial ions increases greatly. Using this interpretation, the conductivity maximum at ~40 to 60% $Li_3YO_4$ ($Y$ = P, As, V), is associated with the changeover in crystal structure from a $Li_4SiO_4$ to a $\gamma$ solid solution: the former is a vacancy conducting system and the latter an interstitial conducting system. This, however, leaves us with the tantalizing uncertainty as to what would happen if either solid solution series was considerably more extensive. Would the conductivity tend to level off at a constant high value or would it still pass through a maximum at ~40–60% $Li_3YO_4$? There is some evidence in support of the latter hypothesis in which case the observed conductivity data may be interpreted as follows.

Structural differences between $Li_4SiO_4$ and $\gamma$ solid solutions are assumed to be unimportant. This seems reasonable as a first approximation since both have a similar oxide ion array that is intermediate between tetragonal packed and hexagonal close-packed (*19*); hence, similar conduction pathways are probably available to the $Li^+$ ions in the two structures. It has to be assumed that, on addition of interstitial $Li^+$ ions to $Li_3$(P, As, V)$O_4$, only one extra $Li^+$ ion per formula unit can be accommodated in the particular set of sites that is favored. Thus, in $Li_4SiO_4$ these sites are essentially fully occupied whereas in $Li_3$(P, As, V)$O_4$ they are empty. Further, it has to be assumed that, in order for conduction to occur, these sites must be only partially occupied. A recent redetermination of the structure of $Li_4SiO_4$ (*21*) has shown it to possess a weak superstructure. The lithium atoms are ordered into 19 out of 42 possible sites in the supercell. It was concluded (*21*) that the high conductivity of solid solutions such as $Li_4SiO_4$–$Li_3PO_4$ is due to the good 3D connectivity between Li sites (also present in $Li_4SiO_4$) and to the introduction of either vacancies or interstitials.

An expression for conductivity that is often used is provided by random-walk theory. In this the conductivity $\sigma$ is given by

$$\sigma = Nc(1 - c)e^2a^2\gamma\omega_0k^{-1}T^{-1}\exp(-\Delta G/kT)$$

in which $e$, $a$, $\gamma$, $\omega_0$, $k$, $T$ and $G$ are the electronic charge, the jump distance for the ions, a constant depending on the number of possible jumps available to a particular ion, the vibrational frequency of the mobile ions, Boltzman's constant, absolute temperature, and the free energy of activation for migration. The key term of present interest is the product $Nc(1 - c)$. $N$ is the number of equivalent sites and $c$ is the concentration of ions on these sites. If $c$ is either 0 or 1 the product $Nc(1 - c)$ is zero; if $c$ = 1/2, the product has a maximum value. The effect of this product on the preexponential factor $A$ is shown in Fig. 6, by writing the solid solution formulae as $Li_{3+c}(P, V, As)_{1-c}Si_cO_4$. The dashed curve is given by $c(1 - c)A'$ in which $A'$ has a constant value but is adjusted so that the calculated curve coincides approximately, at the maximum, with the experimental data points for the two systems $Li_4SiO_4$–$Li_3VO_4$ and $Li_4SiO_4$–$Li_3AsO_4$. The experimental data points show considerable scatter, indicative of the errors inherent in measuring preexponential factors accurately. Nevertheless, they do very approximately take the form indicated by the curve.

A brief study was made of the conductivity of ternary $Li_4SiO_4$–$Li_3VO_4$–$Li_3PO_4$ compositions. Samples were prepared on a line with a constant (40%) $Li_4SiO_4$ content.

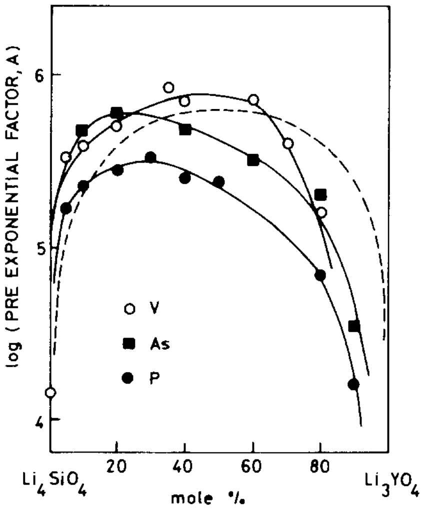

FIG. 6. Influence of the term $c(1 - c)$ on an otherwise constant preexponential factor; dashed line is calculated.

They formed $\gamma$ solid solutions whose formulae may be represented as $Li_{3.4}Si_{0.4}(P_{0.6-y}V_y)O_4$, $y = 0, 0.2, 0.4$, and 0.6. The conductivity of each was measured, as previously, over the range ~20 to 300°C and was found to increase in an approximately linear manner with increasing $y$. Thus, intermediate compositions had a higher conductivity than $Li_{3.4}Si_{0.4}P_{0.6}O_4$ but a lower conductivity than $Li_{3.4}Si_{0.4}V_{0.6}O_4$.

## Conclusions

The three systems $Li_4SiO_4$–$Li_3YO_4$ ($Y$ = P,As,V) show considerable similarities. Each forms two partial solid solution series based on (i) $Li_4SiO_4$ and (ii) $\gamma$-$Li_3YO_4$ end-member structures. In all three systems, the conductivity of the solid solutions is much higher than that of the end members and passes through a broad maximum around the composition $40Li_4SiO_4 \cdot 60\,Li_3YO_4$; of the three, the vanadate system exhibits the highest conductivity. Results on the system $Li_4SiO_4$–$Li_3PO_4$ indicate that although two crystal structure types are observed, the conductivity is not determined primarily by structure type but by the overall $Li^+$ content (*12, 13*). Results on the arsenate and vanadate systems support this conclusion since the conductivity also varies smoothly with composition in these two systems. The similarity in conductivity shown by the two structure types probably arises because they have a similar packing arrangement for the oxide ions. In both, the oxide ion array is intermediate between tetragonal-packed and hexagonal close-packed (*19*) and therefore similar conduction pathways are available to the $Li^+$ ions.

The high conductivity of the solid solutions, as compared to the end members, arises from two causes. First, the activation energy for conduction decreases to a minimum at intermediate solid solution compositions. The reasons for this are not known. Unit cell volumes vary smoothly with composition; the volume increases on addition of $Li_3(V, As)O_4$ to $Li_4SiO_4$ but decreases on addition of $Li_3PO_4$ to $Li_4SiO_4$. There is no obvious correlation between unit cell volume (and site dimensions) and activation energy therefore. Possibly, cooperative interactions between the mobile $Li^+$ ions could act to reduce the activation energy for migration, as has been shown to occur in Na $\beta$-alumina (*20*). Second, the Arrhenius preexponential factor passes through a maximum at intermediate compositions (if the data for $Li_4SiO_4$ above 300°C are excluded). This is attributed to a variation with composition in the number of mobile $Li^+$ ions. For $Li_4SiO_4$ below 300°C, less than 1% of the $Li^+$ ions are mobile but this number increases by between 1 and 2 orders of magnitude in the solid solutions. The mobile carrier concentration in the $Li_3YO_4$ end-member phases is also small. A simplified explanation of the variation of preexponential factor with composition has been given in terms of random-walk theory in which the main variable is the term $c(1 - c)$.

Comparison of the three systems with $Y$ = P, As, V shows that, for a given highly conducting composition, e.g., $40Li_4SiO_4 \cdot 60Li_3YO_4$, the magnitude of the conductivity is in the sequence

$$\sigma_P \lesssim \sigma_{As} < \sigma_V.$$

Analysis of the Arrhenius parameters shows that $A_P < A_{As} < A_V$ and $E_P > E_{As} \gtrsim E_V$. The higher conductivity of the vanadate system is attributed both to its slightly higher preexponential factor and somewhat lower activation energy, therefore.

## Acknowledgment

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