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Ionic conductivity of oxides based on Li_4SiO_4

A. R. WEST

University of Aberdeen, Department of Chemistry, Meston Walk, Old Aberdeen, Scotland

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Lithium orthosilicate, Li_4SiO_4, and its solid solutions are a new group of solids of high ionic conductivity. Either Li or Si may be at least partially replaced by several other di-, tri- or tetra-valent cations. Highest conductivities were found for solid solutions with Si partially replaced by Ti; typical values were 10^{-3} to 10^{-4} Ω^{-1} cm^{-1} at 300°C rising to *c.* 1 Ω^{-1} cm^{-1} by 700°C. The solid solutions are easy to prepare and are stable in air. Conductivities were measured on pressed cubes of powdered material using variable frequency a.c. methods. The conductivities of these Li_4SiO_4 solid solutions are compared with those of other known Li-conducting solids; Li_4SiO_4 solid solutions are probably the best all-round, polycrystalline Li-electrolytes yet found for temperatures above *c.* 200°C.

1. Introduction

With the increasing interest in solid state electrochemical devices, there is growing demand for more compounds which exhibit high ionic conductivity. Existing lithium-ion conductors have been reviewed by Pizzini [1]. These are limited to three main groups (a) lithium halides, (b) Li_2SO_4 and Li_2WO_4 above their transition temperatures, and (c) lithium-substituted β-alumina and other compounds with layer or tunnel structures.

The conductivity of Li_4SiO_4 has so far received little attention. Preliminary studies, using rather crude d.c. measurements, gave a value of *c.* $10^{-2}\Omega^{-1}cm^{-1}$ for the specific conductance at 600°C [2]. In the present report, the crystal chemistry of Li_4SiO_4 is reviewed, together with its ability to form solid solutions containing a wide variety of cations. a.c. conductivity data for Li_4SiO_4 and various solid solution compositions are presented.

2. Crystal chemistry of Li_4SiO_4 and related phases

Li_4SiO_4 exists in two polymorphic forms which are separated by a broad transition region between *c.* 600° and 725°C [3]. The crystal structure of the low temperature form is known [4]. It has a monoclinic unit cell and is a rather complex structure. The oxygens form buckled layers but they do not approximate to a close-packed arrangement. Silicon is tetrahedrally co-ordinated to oxygen and the structure is a typical orthosilicate with isolated $(SiO_4)^{4-}$ groups. The lithiums occupy a variety of sites: the unit cell contains eight lithiums and these are distributed over a total of eighteen 4-, 5- and 6- co-ordinate sites. Thus the sites are only partially occupied by lithium. Because of the large number of lithium sites in the unit cell, the (LiO_n) polyhedra, $n = 4, 5, 6$, are often linked together by sharing common faces. There are six distinct sets of sites occupied by lithium. Four of these, labelled Li(1) - - - Li(4) in the original report [4], have a distorted tetrahedral environment. The other two, Li(5) and Li(6), have 5 and 6 oxygen near-neighbours, respectively, although the polyhedra so formed are rather irregular. The manner and degree with which the different polyhedra share faces may be summarized as follows:

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Polyhedron	*Fractional occupancy*	*Shares common faces with the polyhedra of:*
$Li(1)O_4$	$\frac{2}{3}$	Li(4), Li(5), Li(6), Li(6′)
$Li(2)O_4$	$\frac{1}{2}$	Li(3)
$Li(3)O_4$	$\frac{1}{2}$	Li(2), Li(5), Li(5′), Li(6)
$Li(4)O_4$	$\frac{1}{3}$	Li(1)
$Li(5)O_5$	$\frac{1}{3}$	Li(1), Li(3), Li(5′)
$Li(6)O_6$	$\frac{1}{3}$	Li(1), Li(1′), Li(3)

Note: Li(6′) etc., refers to a Li(6) atom on an equivalent site in the same, or in a neighbouring unit cell.

Thus, the (LiO_n) polyhedra link up by sharing common faces to form a three-dimensional network. The distances between lithiums in pairs of adjacent polyhedra which are connected by a common face are rather short, varying from 0·847±0·074Å for Li(5)−Li(5′) to 1·875±0·079Å for Li(3)−Li(6). With such short distances it is unlikely that both polyhedra of each pair with a common face will be occupied simultaneously; hence the partial occupancies.

The crystal structure of the high temperature form of Li_4SiO_4, which cannot be preserved metastably to ambient temperatures, is not known. However, its X-ray powder pattern at *c.* 800°C is quite similar to that of the low-temperature form of Li_4SiO_4 at room temperature and the two structures are probably closely related. The low-high transition is complex; it appears to be continuous and to take place over a range of temperatures, as shown by continuously-recorded, high-temperature Guinier X-ray powder photographs. However, several peak maxima are observed by DTA in the range 600–725°C, during both heating and cooling cycles, which indicates that the transformation probably occurs in several successive stages [2].

Li_4TiO_4 and Li_4GeO_4 are dimorphic; their high temperature forms are isostructural with each other and with high temperature Li_4SiO_4 [3]. Complete solid solution is presumed to occur within the ternary system bounded by the high-temperature forms of Li_4SiO_4, Li_4GeO_4 and Li_4TiO_4; it has been shown to be complete at high temperatures across the binary edges Li_4SiO_4-Li_4GeO_4 and Li_4GeO_4-Li_4TiO_4 [3].

The low-temperature polymorphs of Li_4GeO_4 and Li_4TiO_4 are also isostructural but are different from the low-temperature form of Li_4SiO_4. Instead, the lithium ions are all 4-coordinate and the lithium sites are fully occupied [5, 6]. Comparison of the two structure-types shows that the (GeO_4) tetrahedra are rotated by a few degrees relative to the (SiO_4) tetrahedra. This causes a change in the shape, size and availability of sites for lithium. Some lithiums in Li_4GeO_4 occupy a set of sites corresponding to Li(1) and Li(3) in Li_4SiO_4, but the other lithiums occupy sites which are completely empty in Li_4SiO_4. There is no sharing of polyhedral faces in Li_4GeO_4.

The low-temperature forms of Li_4SiO_4 and Li_4GeO_4 (or Li_4TiO_4) exhibit considerable mutual solid solubility and are separated only by narrow miscibility gaps [3]. The range of low-temperature Li_4SiO_4 solid solution at 25°C in the two binary systems extends to 56±3 mole % Li_4GeO_4 and 50±5 mole % Li_4TiO_4, respectively. The phase diagram for the system $Li_4SiO_4 - Li_4GeO_4$ is shown in Fig. 1. Phase relations in the system $Li_4SiO_4 - Li_4TiO_4$ have not been fully established but are probably similar to those in the corresponding germanate system.

The high and low-temperature forms of Li_4SiO_4 are capable of taking other cations into solid solution, not only by replacing silicon but also by partially replacing lithium. Phase equilibria in the systems $Li_4SiO_4 - Zn_2SiO_4$ and $Li_4SiO_4 - Mg_2SiO_4$ have been studied [2, 7, 8]. In both systems, Li_4SiO_4 forms a considerable range of solid solutions whose extent increases gradually with rising temperature. Limiting solid solution compositions at 400°C are estimated as $Li_{3\cdot 28}Zn_{0\cdot 36}SiO_4$ [7] and $Li_{2\cdot 96}Mg_{0\cdot 52}SiO_4$ [8], respectively. The crystal structures and polymorphic behaviour of these solid solutions have not been fully established. In both systems, the temperature of the low-high transition range in Li_4SiO_4 falls gradually with increasing solid solution and extra superstructure reflections appear below *c.* 400°C in the powder X-ray patterns of the more Zn- (and Mg-) rich compositions.

Li_4SiO_4 can also take aluminium into solid solution along the join $Li_4SiO_4 - LiAlSiO_4$; the limiting composition for solid solution formation at *c.* 600°C is ($Li_{3\cdot 64}$ $Al_{0\cdot 12}$) SiO_4 [9]. With increasing Al content, the low-high transition in Li_4SiO_4 appears to fade out on DTA, and no superstructure X-ray reflections are observed at low temperatures.

It is quite likely that other small divalent and trivalent cations will be able to enter the Li_4SiO_4 structure. The mechanism of solid solution formation can be formulated nominally as $n\text{Li}^+ \rightleftharpoons \text{M}^{n+} + (n-1)$ vacancies, for replacement of lithium, and as $\text{Si}^{4+} \rightleftharpoons \text{Ge}^{4+}, \text{Ti}^{4+}$ for replacement of silicon. However, the change in fractional occupancy of the various lithium sites in the low-temperature form of Li_4SiO_4, with solid solution composition, cannot be determined so easily. The lithium site occupancies will probably vary in a different manner along each solid solution series and in order to know the occupancies for any particular composition, full refinement of the structure of a single crystal of that composition would be needed.

3. Experimental

Conventional solid state preparative techniques were used. Starting materials were Li_2CO_3 (reagent grade), SiO_2 (very pure crushed crystal quartz, supplied by Thermal Syndicate Ltd.), TiO_2 (very pure, British Titan Products), GeO_2 (electronic grade, Koch–Light Laboratories), ZnO, MgO, Al_2O_3 (Analar). Compositions (5–10 gm) were mixed in an agate mortar as an ethanol-containing paste and mixing continued until all the ethanol had evaporated (10–15 min). Mixtures were fired in gold foil boats at 600–900°C in electrically-heated muffle furnaces for 12–24 h. The sintered products were crushed and refired several times in order to complete reaction. All compositions, apart from those containing zinc were prepared in this way. Zinc-containing solid solutions were prepared in two stages; samples of Li_4SiO_4 and Zn_2SiO_4 were first prepared, and these were mixed in the appropriate proportions and reacted. Compositions were checked for completeness of reaction by recording their powder X-ray patterns with a Guinier–de Wolff focusing camera; relevant powder data are given in the literature [2, 6, 7, 8].

For the conductivity measurements, blocks of powdered material of approximately cubic dimensions, with side = 0·65 cm, were pressed at 50 000–100 000 psi. Some cubes were placed in furnaces at *c.* 1000°C to sinter the particles and reduce porosity, whereas other cubes were used as pressed. However, the sintering treatment did not cause any marked improvement in conductivity relative to unsintered cubes. Platinum tape electrodes were attached to a pair of opposite cube faces using gold paste No. 9177 supplied by Engelhard Ltd. The paste was allowed to dry in air overnight, although it did not harden until subsequently heated to *c.* 200°C. It had been found previously that platinum paste was attacked by lithia in the cubes when heated to *c.* 500°C, with the formation of yellow-green Li_2PtO_3; however, gold showed no signs of attack up to at least 800°C.

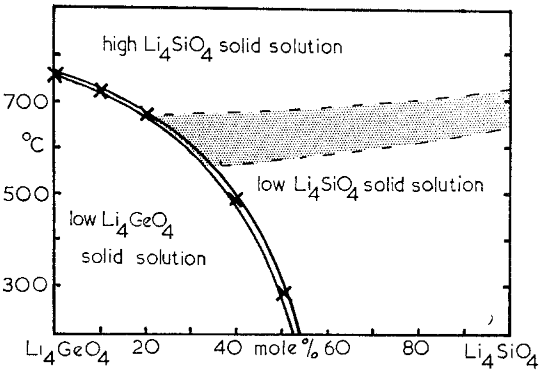

Fig. 1. Subsolidus phase equilibria in the system Li_4SiO_4-Li_4GeO_4. Data are taken from [3]. The stippled region represents the broad transformation range between the low and high-temperature form of Li_4SiO_4 solid solutions.

Each cube, with electrodes attached, was supported by placing it in a channel cut out of a ceramic brick and the platinum tapes passed out through holes in the brick. The tapes were in an approximately parallel arrangement with the leads separated by *c.* 1 cm. The system was made more rigid by fixing the tapes at their entrance to the brick with alumina cement. A schematic diagram of the 'cell' is given in Fig. 2. The cell was placed in an electrically-heated muffle furnace with the Pt leads threaded through insulating ceramic sheaths and passing under the furnace door. With the inaccuracies in the furnace used, reported temperatures are accurate to ±25°C.

Conductivities in air at temperatures ranging from ambient to 750°C were measured with a Wayne Kerr Universal bridge No. B224 operated at a fixed frequency of 1592 Hz. Two-terminal measurements were used, except for conduc-

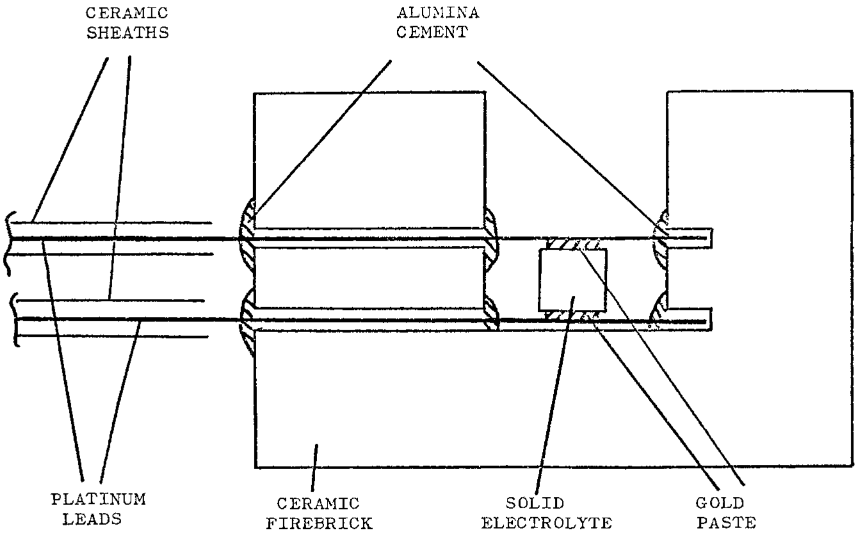

Fig. 2. Schematic section through a conductivity cell.

tivities $>1\times10^{-2}$ Ω^{-1} cm^{-1}, when four-terminal measurements were made. An external Muirhead oscillator in conjunction with the Wayne Kerr bridge was used to measure conductivities over the frequency range 200–30 000 Hz; operating voltages were in the range 0·2 to 1·0 V.

A test was carried out to ensure that the ceramic brick and cement used did not provide an alternate conduction path. For this, a cell was used from which the electrolyte cube had been removed, leaving the leads approximately undisturbed. The conductivity of this blank cell increased from $<10^{-10}$ Ω^{-1} at ambient to 10^{-7} Ω^{-1} by 400°C and 10^{-5} Ω^{-1} at 700°C. These values are several orders of magnitude lower than those of the materials studied here.

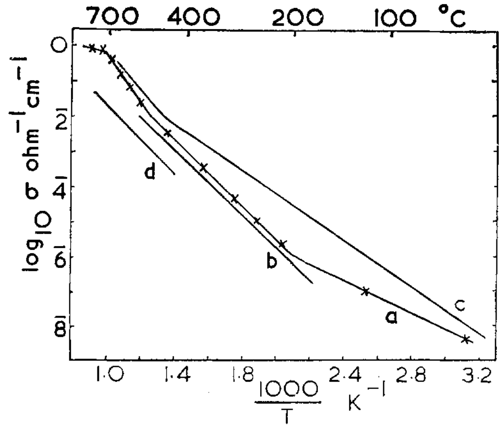

Fig. 3. Plots of $\log_{10}$ conductance versus reciprocal temperature for the following compositions: a = Li_4SiO_4, b = $Li_4(Si_{0.7}Ge_{0.3})O_4$, c = $Li_4(Si_{0.7}Ti_{0.3})O_4$, d = $(Li_{3.4}Zn_{0.3})SiO_4$. Data points for Li_4SiO_4 only are marked. Frequency used was 1592 Hz.

4. Results and Discussion

4.1. *Conductivity measurements*

Conductivity studies were restricted mainly to Li_4SiO_4 and solid solutions which had the Li_4SiO_4 (high or low-temperature form) structure. Initially, the conductivity at fixed frequency (1592 Hz) of several compositions was measured, for temperatures ranging from ambient to *c.* 700°C. Results are given in Figs. 3 and 4. In calculating these conductivities, capacitive effects were ignored. Cell constants (*l*/*A*) were calculated from the 'cube' dimensions, although the pairs of opposite cube faces holding the electrodes were not usually completely covered by the gold paste. The results given were obtained on the heating cycle but were found to be fairly reproducible on cooling or on a second heating cycle. Some of the results showed a considerable scatter but this was probably due to inaccuracies in the control and measurement of temperature. If the cubes were left open to the atmosphere for several days prior to the conductivity measurements, some cubes, especially those rich in titanium, picked up CO_2. This caused a surface

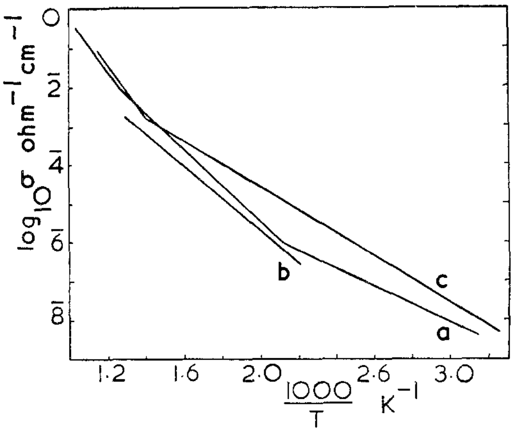

Fig. 4. Plots of $\log_{10}$ conductance versus reciprocal temperature for the following compositions: a = Li_4SiO_4, b = $(Li_{2\cdot8}Zn_{0\cdot6})SiO_4$, c = $Li_4(Si_{0\cdot4}Ti_{0\cdot6})O_4$.

layer of predominantly Li_2CO_3 and Li_2TiO_3 to form, presumably by a reaction such as: $Li_4TiO_4+CO_2 \longrightarrow Li_2CO_3+Li_2TiO_3$. Therefore, all measurements were made on cubes which were only 1–2 days old, in order to reduce the risk of atmospheric attack.

The conducting species is presumed to be Li^+ although the other ions may be mobile to a certain extent.

Substitution in Li_4SiO_4 of Zn for Li or Ge for Si resulted in a lowering of the conductivity at all temperatures, relative to Li_4SiO_4. However, substitution of Ti for Si caused a considerable increase in conductivity; best values were obtained for compositions containing 30 and 40% substituted titanium. With more than 40% titanium, the conductivity decreased and the composition containing 60% substituted titanium had a conductivity comparable to that of Li_4SiO_4. However, this latter titanium-rich composition is a solid solution based on Li_4TiO_4 and not Li_4SiO_4; only at temperatures considerably above ambient does it transform to an Li_4SiO_4 type of structure.

In Fig. 4, data are also given for $(Li_{2\cdot8}Zn_{0\cdot6})SiO_4$, a lithium-rich member of a solid solution series based on Li_2ZnSiO_4. These solid solutions have a structure somewhat like that of Li_4SiO_4 and its zinc-containing solid solutions, but at temperatures up to at least 1000°C, there is a miscibility gap between the two solid solution series [2, 7]. Li_2ZnSiO_4 itself is polymorphic, and in at least two of its polymorphs, lithium is tetrahedrally-co-ordinated and the sites are fully occupied. However, in the lithium-rich solid solutions of Li_2ZnSiO_4, it is not known which sites are occupied by the excess lithiums nor whether the occupancy of these sites is only partial.

The solid solutions containing titanium were chosen for further investigation as, of the various solid solutions derived from Li_4SiO_4 which were studied, these had the highest conductivities. The frequency-dependence of the conductivity for several titanium-containing solid solutions was measured at different temperatures; results are given in Figs. 5 and 6. For these figures, the conductivities (and capacitances) used were the indicated bridge values. No corrections were made for the equivalent electrical circuit of the cell being other than a parallel RC arrangement. This may lead to errors, especially at high temperatures, as for most compositions and temperatures studied, the resistance and capacitance were found to be frequency-dependent showing that the equivalent cell circuit is not simply parallel RC or series RC.

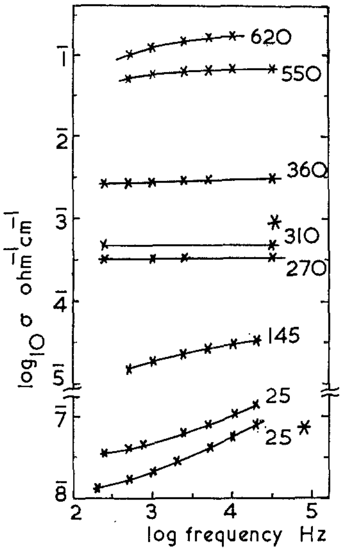

Fig. 5. Plots of $\log_{10}$ conductance versus $\log_{10}$ frequency for two compositions: $Li_4(Si_{0\cdot7}Ti_{0\cdot3})O_4$ (marked with an asterisk) and $Li_4(Si_{0\cdot6}Ti_{0\cdot4})O_4$. Numbers on each curve are temperatures in °C.

All the compositions studied showed a considerable frequency dependence at ambient, with conductivities increasing by half to one order of

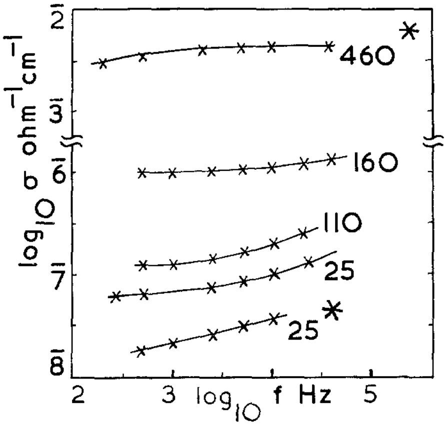

Fig. 6. Plots of $\log_{10}$ conductance versus $\log_{10}$ frequency for two compositions: $Li_4(Si_{0\cdot4}Ti_{0\cdot6})O_4$ (marked with an asterisk) and $Li_4(Si_{0\cdot85}Ti_{0\cdot15})O_4$. Temperatures are in °C.

magnitude over the frequency range 200 to 30 000 Hz. Indicated capacitances were usually several picofarads and decreased slowly with increasing frequency. At higher temperatures, the frequency dependence of the conductivity became progressively less until at temperatures around 300°C, the conductivities, with values of *c.* $10^{-3}\ \Omega^{-1}\ cm^{-1}$, were virtually independent of frequency. At these temperatures, capacitances fell rapidly from several nanofarads to several picofarads with increasing frequency.

At temperatures above *c.* 400°C, conductivities again became frequency-dependent and this dependence increased with rising temperature. For $Li_4(Si_{0\cdot6}Ti_{0\cdot4})O_4$ at 620°C, the conductivity approximately doubled between 500 and 10 000 Hz; the corresponding indicated capacitance fell from 8 μF to 140 nF. The frequency dependence of the conductivity of the composition $Li_4(Si_{0\cdot4}\ Ti_{0\cdot6})O_4$ was somewhat different from the general pattern of frequency dependence but as this composition has the Li_4TiO_4 structure at low temperatures, this is not too surprising.

From Figs. 5 and 6, there appears to be two types of frequency dependence. The high-temperature conductivities tend to level off at progressively higher frequencies and, although the reason for the frequency dependence is not known, it is probably associated with electrode-electrolyte interface effects. These cause a concentration polarization in the electrolyte which only disappears at high frequencies. The low-temperature conductivities tend to level off at progressively lower frequencies and this type of dependence is attributed to relaxation effects. However, further work is clearly needed on both frequency dependencies.

The conductivity of $Li_4(Si_{0\cdot6}Ti_{0\cdot4})O_4$ is shown in Fig. 7. The values used for this plot are

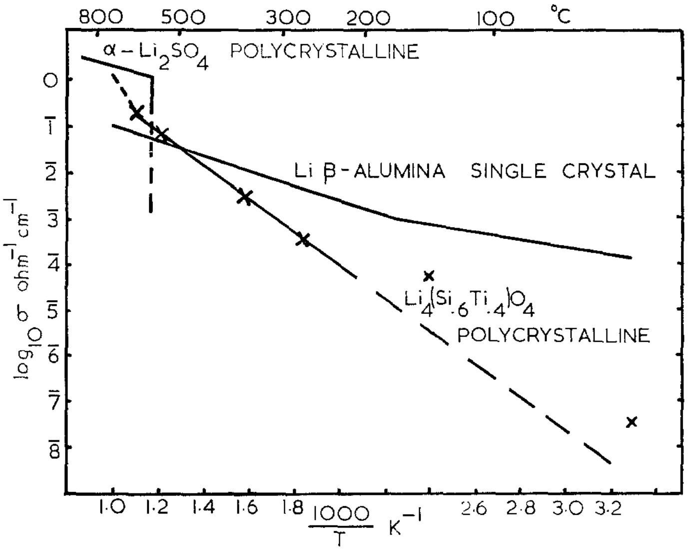

Fig. 7. Plot of $\log_{10}$ conductance vs reciprocal temperature for $Li_4(Si_{0\cdot6}$-$Ti_{0\cdot4})O_4$, α-Li_2SO_4 and Li β-alumina. The increased slope of the extrapolation to higher temperatures for $Li_4(Si_{0\cdot6}Ti_{0\cdot4})O_4$ is schematic and assumes an analogy with Li_4SiO_4. (See discussion of results and Fig. 3.)

taken from the flattest regions of Fig. 5 where the conductivity is least frequency dependent. Also shown for comparison is the conductivity of α-Li_2SO_4 [13] and Li β-alumina [15]. The high temperature results for $Li_4(Si_{0\cdot6}Ti_{0\cdot4})O_4$ fall on a straight line with an activation energy of 79 KJ mole^{-1}; this is considerably higher than the values for α-Li_2SO_4 and lithium β-alumina. The low temperature conductivities of $Li_4(Si_{0\cdot6}Ti_{0\cdot4})O_4$ are rather high and could indicate either incorrect treatment of the results or the presence of extrinsic conductivity.

All the conductivity data reported here were obtained using a.c. measurements. A few tests were tried with one cube to measure its d.c. resistance. Using an Avometer, the initial resistance approached the value obtained by a.c. (20 Ω) but then increased rapidly to several hundred ohms. Similar results were obtained on reversing the leads. In the earlier d.c. measurements on Li_4SiO_4, using platinum electrodes, the resistance was approximately constant with time [2]. However, the platinum electrodes were attacked by lithium from the cubes with the formation of Li_2PtO_3 at the electrolyte/electrode interface. This Li_2PtO_3 must have acted as a non-polarizable electrode, i.e. as both a source and sink of lithiums. Hence the fairly good agreement between those d.c. measurements on Li_4SiO_4 and the present a.c. values.

4.2. *Effects of crystal chemistry on conductivity*

The temperature dependence of the conductivity of Li_4SiO_4 (Fig. 3, curve a) is interesting; a change of slope occurs three times over the range ambient to *c.* 800°C. The first change, at 200°C, is probably associated with the transition from extrinsic to intrinsic conductivity. At 550–600°C a more subtle, but reproducible, change of slope occurs and this new slope continues to *c.* 730°C. Above 730°C the slope is much flatter and, although only limited data are available, it probably continues in this way up to the melting point, 1255°C [11]. At these latter high temperatures, electrode/electrolyte interface effects will be quite important, and the conductivity values obtained may be too low by up to half an order of magnitude. Thus, although the general features of conductivity variation are established, the results above *c.* 600°C are only semi-quantitative.

The changes in slope at 550° and 730°C are directly associated with the broad transition region between the low and high-temperature forms of Li_4SiO_4, which is observed by DTA and high-temperature X-ray powder patterns to occur over the range 600° to 725°C. The crystal structure of the high-temperature form of Li_4SiO_4 is not known but it has been suggested previously that the low-high transition in Li_4SiO_4 mainly involves a change in fractional occupancy of the various lithium sites, with the silicons and oxygens remaining virtually unchanged [3]. The conductivity data are consistent with this theory. There is no dramatic change in conductivity such as occurs at the transition in AgI; rather the conductivity changes smoothly and the transition is spread over 100–150°C. The low-high transition may be thus regarded as a partial order-disorder transition.

The situation in Li_2SO_4 is somewhat similar, but its low-high transition is a reconstructive one and not purely order-disorder in nature [12, 13]. Consequently, its conductivity probably changes by several orders of magnitude at the transition. The high-temperature form of Li_2SO_4 has the spinel structure with lithium disordered over the available tetrahedral sites [14]; its conductivity varies from 0·3 to 3 $\Omega^{-1}cm^{-1}$ over the range 585° to 870°C [13]. Thus, the conductivities of the high-temperature forms of Li_2SO_4 and Li_4SiO_4 are comparable, probably with similar activation energies, but at lower temperatures, the conductivity of Li_4SiO_4 probably decreases more gradually than does that of Li_2SO_4.

Substitution in Li_4SiO_4 of germanium for silicon leads to a drop in conductivity over the range 150° to 550°C, but substitution of titanium for silicon causes the conductivity to rise at all temperatures. In both these solid solutions there is no change in the overall number of Li ions and sites available, as solid solution presumably occurs by a direct $Si \rightleftharpoons Ti$, Ge replacement mechanism. It is interesting to speculate why substitution of two elements, both of which are larger than silicon, should affect the conductivities in opposite ways.

It was originally hoped that, with appropriate choice of substituent, a solid solution based on Li_4SiO_4 could be found in which the low-high transition occurred at temperatures considerably lower than 600–700°C, and that the high conductivities associated with high Li_4SiO_4 would consequently exist at lower temperatures. However, substitution of zinc in Li_4SiO_4, which was known to lower the temperature of the transition range [2], caused the conductivity to fall by approximately an order of magnitude relative to Li_4SiO_4 (Fig. 3).

Li_4SiO_4 itself was found to be very highly conducting above *c.* 720°C and its conductivity increased only gradually with further rise in temperature. Although the conductivity of titanium-containing solid solutions was not investigated above *c.* 620°C, it is expected that these solid solutions will also be more highly conducting at temperatures above their low-high transition zone, *c.* 700°C.

The conductivities of compositions along the join Li_4SiO_4–Li_4TiO_4 are at a maximum around 40 mole % Li_4TiO_4. It is not certain if this is a true maximum along the Li_4SiO_4 solid solutions or whether the maximum coincides with the transition of more titanium-rich compositions to an Li_4TiO_4 solid solution structure, with a correspondingly lower conductivity for the latter solid solutions.

5. Comparison of Li_4SiO_4 solid solutions with other ionic conductors

The Li_4SiO_4-based solid solution with the highest conductivity studied was the composition $Li_4(Si_{0\cdot6}Ti_{0\cdot4})O_4$. Its properties compare very favourably with those of other lithium ion conductors (see Fig. 7). The conductivity is comparable to that of Li_2SO_4 above *c.* 700°C and is probably considerably better below *c.* 600°C: the sharp drop in conductivity at the phase transition in Li_2SO_4 is not observed in $Li_4(Si_{0\cdot6}Ti_{0\cdot4})O_4$.

The conductivity of Li β-alumina has been reported [15]. It appears to be better than the Li_4SiO_4 solid solutions below *c.* 500°C, but the situation reverses at higher temperatures. However, these data are for single crystal specimens with conduction occurring in two-dimensions only, i.e. within the planes between adjacent spinel blocks; the conductivity through the blocks is much lower. Polycrystalline conductivities are expected to be at least an order of magnitude lower than the single crystal values. Thus, $Li_4(Si_{0\cdot6}Ti_{0\cdot4})O_4$ is probably a better conductor than polycrystalline Li β-alumina above *c.* 200°C, as well as being much easier to prepare.

The other lithium ion conductors listed by Pizzini are doped lithium halides; Li_4SiO_4 has superior conductivity to these at all temperatures.

6. Conclusions

Li_4SiO_4 and its solid solutions are an important new group of highly conducting solids, belonging to the class of so-called superionic conductors. They appear to be the best all-round, polycrystalline Li-ion conductors yet known, for temperatures above *c.* 200°C. Particularly advantageous is their ease of preparation and stability in air, especially at high temperatures.

The conductivities are sensitive to solid solution composition as well as temperature and the highest values found were when Ti partially replaced Si. It is quite possible that other solid solutions will be found with still higher conductivity; in particular, the substitution of monovalent cations may enhance the conductivity.

The crystal structure of low Li_4SiO_4 shows that the lithium-oxygen polyhedra, which represent the lithium sites, are connected together by multiple sharing of faces to form a three-dimensional network of cages linked by triangular windows. On average, the lithium sites are less than half full and so there are plenty of available sites for a hopping conduction mechanism. There are also plenty of other sites which are unoccupied according to the crystal structure analysis, but which could be occupied transiently and so afford extra conduction pathways. However, more work is needed in order to better understand the transport processes.

Acknowledgements

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