

## FAST Li IONIC CONDUCTION IN SOLID SOLUTIONS OF THE SYSTEM $\text{Li}_4\text{GeO}_4\text{--Li}_2\text{ZnGeO}_4\text{--Li}_3\text{PO}_4$

J.G. KAMPHORST and E.E. HELLSTROM\*

*Department of Solid State Chemistry, Physics Laboratory, State University of Utrecht,  
3508 TA Utrecht, The Netherlands*

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A wide range of solid solution formation in the  $\text{Li}_4\text{GeO}_4\text{--Li}_2\text{ZnGeO}_4\text{--Li}_3\text{PO}_4$  system was observed to occur with a structure based on  $\gamma\text{II--Li}_3\text{PO}_4$ . This includes the fast Li conductor lisicon ( $\text{Li}_{14}\text{Zn}(\text{GeO}_4)_4$ ). The ionic conductivities of solid solutions in this system are reported. Much of the solid solution range is structurally metastable at room temperature; however, the decomposition kinetics are appreciable only at elevated temperatures ( $> 350^\circ\text{C}$ ). The evolution of low  $\text{Li}_4\text{GeO}_4$  on decomposing causes an irreversible decrease in the conductivity. At  $200^\circ\text{C}$ , the bulk ionic conductivity of several of these solid solutions is higher than that of lisicon. Solid solutions along the  $\text{Li}_4\text{GeO}_4\text{--Li}_3\text{PO}_4$  tie line are structurally stable and have a higher bulk ionic conductivity than lisicon, and also of the corresponding  $\text{Li}_4\text{SiO}_4\text{--Li}_3\text{PO}_4$  solid solutions at  $200^\circ\text{C}$ .

### 1. Introduction

Recently, Hong [1] reported on Li ionic conductivity in material of composition  $\text{Li}_{16-2x}\text{D}_x(\text{TO}_4)_4$ ,  $\text{D} = \text{Zn, Mg; T} = \text{Si, Ge; } 0 < x < 4$ . He indicated that within each of these systems a continuous solid solution was formed for  $0 < x < 4$ , and that the same crystal structure was adopted by all four systems. Of these solid solution electrolytes, the composition  $\text{Li}_{14}\text{Zn}(\text{GeO}_4)_4$ , which Hong [1] singled out to be named lisicon, for lithium superionic conductor, exhibits the highest lithium conduction known between  $300$  and  $400^\circ\text{C}$ . Hong [1] also determined the structure of lisicon, and proposed a pathway for Li conduction.

Von Alpen et al. [2] studied lisicon using ac conductivity methods, and dc ionic four-probe techniques. They observed conductivity values about an order of magnitude lower than those observed by Hong. They also found lisicon to be unstable in contact with Li metal at  $200^\circ\text{C}$ .

The ionic conductivity of  $\text{Li}_4\text{GeO}_4$  has been reported to be quite low ( $10^{-4}$  S

\* Present address: Department of Inorganic Chemistry, Analytical Chemistry Laboratory, State University of Utrecht, 3522 AD Utrecht, The Netherlands.

m<sup>-1</sup> at 200°C)[3–5]. West and Glasser [6] found that the  $\gamma$ -form of Li<sub>2.2</sub>Zn<sub>0.9</sub>SiO<sub>4</sub> conducts better than the  $\beta$ -form, but that both are poor ionic conductors, so the isostructural Li<sub>2</sub>ZnGeO<sub>4</sub> might be expected to be a poor conductor as well. Surprisingly, lisicon which is isostructural with  $\gamma_{II}$ -Li<sub>2</sub>ZnSiO<sub>4</sub>, and lies on the tie line between the low conductivity germanate phases, exhibits a very high ionic conductivity. This behaviour can be compared with solid solutions in the Li<sub>4</sub>SiO<sub>4</sub>–Li<sub>3</sub>PO<sub>4</sub> system, where the terminal phases are poor ionic conductors, while dramatic conductivity increases have been reported for the solid solutions based upon them [7–9].

As the high-temperature  $\gamma_{II}$ -form of Li<sub>3</sub>PO<sub>4</sub> and lisicon are isostructural, solid solution formation between Li<sub>3</sub>PO<sub>4</sub> and lisicon is expected to occur, leading to new Li electrolytes. A brief investigation of several compositions along the Li<sub>4</sub>GeO<sub>4</sub>–Li<sub>3</sub>PO<sub>4</sub> tie line was also carried out.

In this article we report electrical conductivity and structural data for solid solutions in the Li<sub>4</sub>GeO<sub>4</sub>–Li<sub>2</sub>ZnGeO<sub>4</sub>–Li<sub>3</sub>PO<sub>4</sub> system.

## 2. Crystal chemistry relevant to the Li<sub>4</sub>GeO<sub>4</sub>–Li<sub>2</sub>ZnGeO<sub>4</sub>–Li<sub>3</sub>PO<sub>4</sub> system

Many of the phases Li<sub>4</sub>TO<sub>4</sub>, Li<sub>2</sub>DTO<sub>4</sub> and Li<sub>3</sub>MO<sub>4</sub> where D = Mg<sup>2+</sup>, Ca<sup>2+</sup>, Fe<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>; T = Si<sup>4+</sup>, Ge<sup>4+</sup>, Ti<sup>4+</sup>; M = P<sup>5+</sup>, As<sup>5+</sup>, V<sup>5+</sup>, Cr<sup>5+</sup>, Mn<sup>5+</sup> are known to exist [10,11]. No Li<sub>2</sub>DTiO<sub>4</sub> phases are known to date, possibly because Ti<sup>4+</sup> does not easily adopt tetrahedral coordination.

In general, the stable phases have a distorted hexagonal close packing of oxygen, with the cations in tetrahedral sites. However, due to a high amount of distortion in Li<sub>4</sub>SiO<sub>4</sub>, some Li are 5 and 6 coordinated by oxygen. The structures of the phases above may be divided into two groups, with the Li<sub>2</sub>DTO<sub>4</sub> and Li<sub>3</sub>MO<sub>4</sub> phases in one group and the Li<sub>4</sub>TO<sub>4</sub> phases in the other.

In the former group, where D occupies the same tetrahedral sites as Li, two main polymorphs are formed, the low-temperature  $\beta$ -form, and the high-temperature  $\gamma$ -form. The kinetics of the  $\gamma \rightarrow \beta$  transition are rather sluggish, so in many instances the  $\gamma$ -form could be quenched to room temperature [6,12].

The structural data for lisicon reveal that it is isostructural with  $\gamma_{II}$ -Li<sub>3</sub>PO<sub>4</sub>. Hong [1] determined the crystal structure of single crystalline lisicon, but since each system Li<sub>16-2x</sub>D<sub>x</sub>(TO<sub>4</sub>)<sub>4</sub>, D = Zn, Mg; T = Si, Ge, forms a complete solid solution for 0 < x < 4, all having the same crystal structure, the basic description of the lisicon structure holds for all of these compositions. In the lisicon structure, which is made up of a three-dimensional network composed of Li<sub>11</sub>Zn(GeO<sub>4</sub>)<sub>4</sub>, partial occupancy by the three remaining Li ions of two additional sites with site symmetry 4a and 4c in space group Pnma occurs [1]. Hong [1] asserts that these three Li ions are the mobile ions.

From the pseudoternary Li<sub>4</sub>GeO<sub>4</sub>–Li<sub>2</sub>ZnGeO<sub>4</sub>–Li<sub>3</sub>PO<sub>4</sub> phase diagram shown in fig. 1, it is seen that the Li and Zn content within solid solutions incorporating Li<sub>3</sub>PO<sub>4</sub> can be individually or simultaneously varied relative to the Li<sub>11</sub>Zn(GeO<sub>4</sub>)<sub>4</sub> framework.

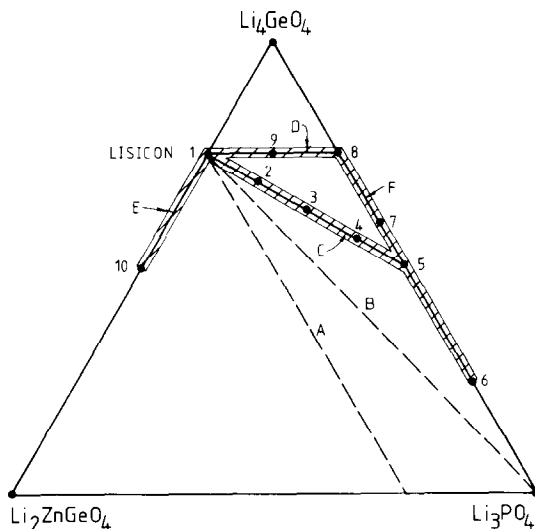


Fig. 1. The  $\text{Li}_4\text{GeO}_4\text{-Li}_2\text{ZnGeO}_4\text{-Li}_3\text{PO}_4$  ternary system showing compositions 1–10. Hatched region denotes initial  $\gamma$ -structure solid solution. Lines: A = constant Zn content; B = lisicon– $\text{Li}_3\text{PO}_4$  tie line; C = constant total Li; D = constant mobile Li (4a and 4c sites); all referred to a constant  $\text{Li}_{11}\text{Zn}(\text{GeO}_4)_4$  network.

Whereas Hong [1] reports solid solution formation in the systems  $\text{Li}_{16-2x}\text{D}_x(\text{TO}_4)_4$ ,  $\text{D} = \text{Zn, Mg}$ ;  $\text{T} = \text{Si, Ge}$ ,  $0 < x < 4$ , West and Glasser [6,13] report that in the  $\text{Li}_4\text{SiO}_4\text{-Li}_2\text{ZnGeO}_4$  system a continuous  $\gamma_{\text{II}}$ -type solid solution forms over the composition range  $1.88 \leq x \leq 4$  above  $\approx 900^\circ\text{C}$ , but that at lower temperatures, portions of this solid solution begin to structurally decompose into two phases. For the composition  $\text{Li}_{14}\text{Zn}(\text{SiO}_4)_4$ , above  $\approx 700^\circ\text{C}$ , a one-phase material forms with the high  $\text{Li}_4\text{SiO}_4$  structure, which decomposes to low  $\text{Li}_4\text{SiO}_4$  plus a  $\gamma$ -type phase at room temperature.

In the  $\text{Li}_4\text{SiO}_4\text{-Li}_3\text{PO}_4$  system, Hu et al. [8] report two regions of solid solution formation. One is based on the low  $\text{Li}_4\text{SiO}_4$  structure from 0 to  $\approx 50$  m/o  $\text{Li}_3\text{PO}_4$ , and the other on the  $\gamma_{\text{II}}\text{-Li}_3\text{PO}_4$  structure from  $\approx 50$  to 100 m/o  $\text{Li}_3\text{PO}_4$ .

### 3. Experimental considerations

Samples with compositions as shown in fig. 1 were prepared from high-purity  $\text{Li}_2\text{CO}_3$  (Merck, P.A.),  $\text{ZnO}$  (Baker, 99.8%),  $\text{GeO}_2$  (U.C.B., Tout Pur) and  $(\text{NH}_4)_2\text{HPO}_4$  (Merck, P.A.).

Following Hong's stoichiometric preparation [1] yielded a two-phase sample due to lithia loss. This was compensated for by adding an extra 10% of  $\text{Li}_2\text{CO}_3$ . The powders were mixed by ball-milling, and fired for about 16 h at  $1100^\circ\text{C}$  in air, fol-

lowed by subsequent ball-milling, cold pressing of disc shaped pellets and sintering. Sintering times were 10–120 min, at temperatures from 1150 to 1230°C in air. After sintering, the pellets were cooled to room temperature in about 2 h. Pellet densities ranged from 76 to 87% of theoretical.

X-ray diffraction patterns were obtained using Cu K $\alpha$  radiation (Philips XRD) with KCl added to provide an internal standard for lattice parameter determination.

The samples were provided with sputtered Pt electrodes, as von Alpen et al. [2] reported that a reaction between Mo or Cr/Au electrodes leads to an irreversible decrease in the conductivity, while reproducible results were obtained with Pt electrodes. For the ac conductivity measurements, the sample was spring loaded between Pt discs in a stainless steel conductivity cell. Nitrogen was typically used as the ambient atmosphere. A detailed description of the conductivity bridges employed has been reported elsewhere [14]. Admittance parameters were measured in the temperature range 25–450°C over the frequency range  $10^{-3} - 5 \times 10^4$  Hz with a signal of 50–100 mV rms.

#### 4. Results

The lattice parameters of compositions 1–10 were fitted by starting with the orthorhombic lisicon indexing, followed by use of a refining and four-parameter least-squared-error fit program [15]. The lattice parameters given in table 1 vary continuously along each of the tie lines shown in fig. 1.

A slight monoclinic distortion was observed throughout the system, including a slight distortion for lisicon itself. The angles for all the solid solutions were approximately equal to or smaller than the angle in monoclinic Li<sub>4</sub>GeO<sub>4</sub> (90.2°) [16] as expected.

Also shown in table 1 are the phases present for selected compositions before and after conductivity measurements.

An example of the ac conductivity response plotted in the complex admittance plane is shown in fig. 2. In the frequency range employed, portions of two semicircles appear, each centered below the abscissa.

The equivalent circuit shown in fig. 2 was used to fit the high frequency semicircular portion of the plots.  $C_G$  is the geometric capacitance,  $R_B$  is the ionic bulk resistance, and  $R_{GB}$  is the grain-boundary-transfer resistance. The Warburg-like diffusional impedance  $Z_{GB}$  is of the form  $A(i\omega)^{-\alpha}$ , where  $0 < \alpha < 1$ , and is thought to be related to ionic transfer from grain to grain. Results of fitting the data in fig. 2 with this circuit are included in the same figure, along with numerical values for the circuit elements.

The sample conductance  $G$  corresponding to the common abscissa intersection point between the two semicircles is given by

$$G = (R_B + R_{GB})^{-1}, \quad (1)$$

Table I  
Lattice parameters, activation enthalpies for conduction and phases present as a function of thermal history for solid solutions 1-10

Solid solution	<i>a</i> <sub>0</sub> (Å)	<i>b</i> <sub>0</sub> (Å)	<i>c</i> <sub>0</sub> (Å)	β (deg)	Δ <i>H</i> (kJ/mole)	Phases present a)	
						before cond. meas.	after cond. meas. b)
1 Li <sub>14</sub> (GeO <sub>4</sub> ) <sub>4</sub>	10.868	6.222	5.168	90.23	63.7	γ + < 5% D	γ + L
2 Li <sub>14</sub> Zn <sub>0.75</sub> (Ge <sub>7/8</sub> P <sub>1/8</sub> O <sub>4</sub> ) <sub>4</sub>	10.835	6.226	5.138	90.09	69.5	γ + < 5% D	-
3 Li <sub>14</sub> Zn <sub>0.5</sub> (Ge <sub>3/4</sub> P <sub>1/4</sub> O <sub>4</sub> ) <sub>4</sub>	10.790	6.215	5.115	90.11	56.0	γ + < 5% D	-
4 Li <sub>14</sub> Zn <sub>0.25</sub> (Ge <sub>5/8</sub> P <sub>3/8</sub> O <sub>4</sub> ) <sub>4</sub>	10.740	6.194	5.093	90.08	49.2	γ + < 5% D	-
5 Li <sub>14</sub> (Ge <sub>0.5</sub> P <sub>0.5</sub> O <sub>4</sub> ) <sub>4</sub>	10.700	6.181	5.060	90.14	48.2	γ	-
6 Li <sub>13.33</sub> (Ge <sub>1/3</sub> P <sub>2/3</sub> O <sub>4</sub> ) <sub>4</sub>	10.650	6.166	5.027	90.10	-	γ	-
7 Li <sub>14.4</sub> (Ge <sub>0.6</sub> P <sub>0.4</sub> O <sub>4</sub> ) <sub>4</sub>	10.716	6.193	5.087	90.11	47.3	γ	-
8 Li <sub>15</sub> (Ge <sub>3/4</sub> P <sub>1/4</sub> O <sub>4</sub> ) <sub>4</sub>	10.783	6.199	5.119	90.06	58.8	γ	-
9 Li <sub>14.5</sub> Zn <sub>0.5</sub> (Ge <sub>7/8</sub> P <sub>1/8</sub> O <sub>4</sub> ) <sub>4</sub>	10.833	6.219	5.139	90.21	56.9	γ + < 5% L	γ + 80% L
10 Li <sub>12</sub> Zn <sub>2</sub> (GeO <sub>4</sub> ) <sub>4</sub>	10.885	6.252	5.155	90.08	84.9	γ + < 5% D	γ

a) L = Low Li<sub>4</sub>GeO<sub>4</sub>, D = unidentified Li deficient phase.

b) Above 350°C for 4-16 h.

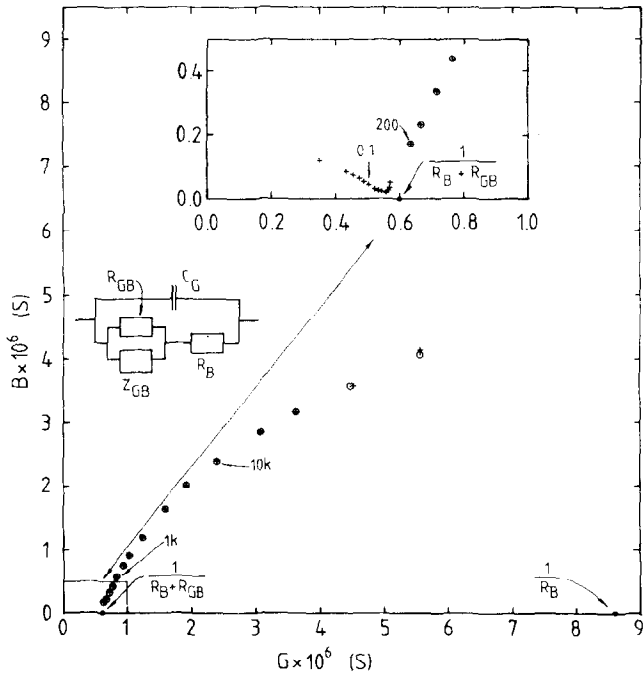


Fig. 2. Experimental data (+) and equivalent circuit data fitting (o) for a sample of composition 9 at 50°C. Inset shows the low frequency response. Values for the equivalent circuit elements extracted from the data fitting are:  $R_B = 1.16 \times 10^5 \Omega$ ,  $R_{GB} = 1.55 \times 10^6 \Omega$ ,  $C_G = 4.9 \text{ pF}$ ,  $Z_{GB} = 9.45 \times 10^8 (\omega)^{-0.74}$ . Frequencies are shown in Hz.

and is plotted for *lisicon* as  $\log(\sigma T)$  versus  $1/T$  in fig. 3. Also included is the bulk conductivity at 50°C, extracted from the data fitting, and an extrapolated bulk conductivity value at 90°C. The data of Hong [1] and von Alpen et al. [2] are included for comparison.

The data from the present study shown in fig. 3 are from the first heating cycle, as above  $\approx 350^\circ\text{C}$ , the sample conductance irreversibly decreased with time. This is the reason why our conductivity data above  $\approx 350^\circ\text{C}$  lie below a linear extrapolation of the low-temperature data. An irreversible decrease in conductivity was found to occur, to differing extents, in compositions 1–4, and 9, while the conductivity of composition 10, and those along the  $\text{Li}_4\text{GeO}_4\text{-Li}_3\text{PO}_4$  tie line remained constant on temperature cycling. Therefore, the conductivity data presented here are those measured during the initial heating.

A conductivity isotherm at 200°C is shown in fig. 4 for the compositions measured in this study. This temperature was selected as here the metastable compositions had not decomposed to any appreciable extent. The *lisicon* datum of von Alpen et al. [2] as well as the data of Ilu et al. [8] for compositions in the  $\text{Li}_4\text{SiO}_4\text{-}$

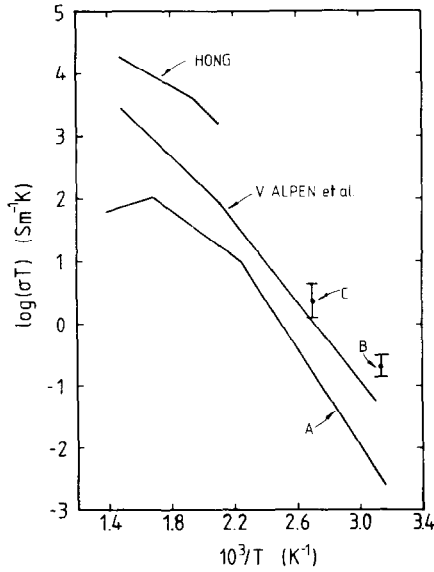


Fig. 3. Conductivity in lison plotted as  $\log(\sigma T)$  versus  $1/T$ . A, sample conductance  $G$  from this study measured during the initial heating. B, bulk ionic conductivity at  $50^\circ\text{C}$  extracted from equivalent circuit data fitting. C, bulk ionic conductivity at  $90^\circ\text{C}$  extrapolated from complex admittance plot. Data of Hong [1] and von Alpen et al. [2] are shown for comparison.

$\text{Li}_3\text{PO}_4$  system have been added for comparison. Collected in table 1 are the activation enthalpies for the sample conductance  $G$  of compositions 1–10.

The electronic conductivity of the samples in a nitrogen atmosphere, found by extrapolating the low-frequency admittance data to 0 Hz, was only observable at

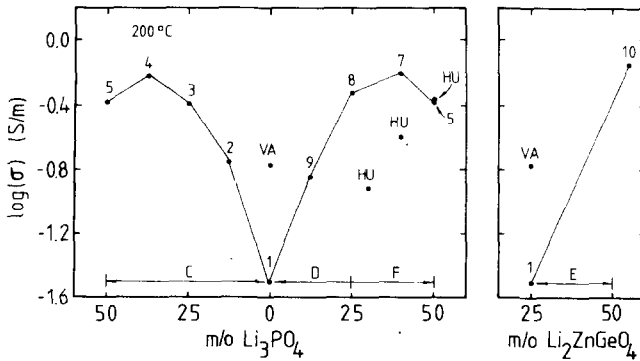
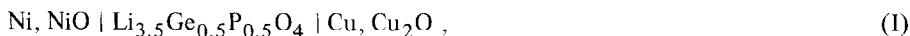


Fig. 4. Conductivity isotherm at  $200^\circ\text{C}$  for compositions 1–10. Data plotted as a function of  $m/o \text{Li}_3\text{PO}_4$  or  $m/o \text{Li}_2\text{ZnGeO}_4$  along the lines in fig. 1. VA = lison data of von Alpen et al. [2]. HU = data for corresponding compositions in the  $\text{Li}_4\text{SiO}_4\text{-Li}_3\text{PO}_4$  system after Hu et al. [8].

the highest temperatures (400–450°C), and was only a few tenths of a percent of the ionic conductivity. With an oxygen partial pressure of 1 atm, the electronic conductivity increased by about a factor of 4. An estimate of the electronic transference number with a controlled low oxygen partial pressure at the electrodes yielded  $t_e < 10^{-5}$  in Li<sub>3.5</sub>Ge<sub>0.5</sub>P<sub>0.5</sub>O<sub>4</sub> at 300°C. This was done by measuring the EMF and current-voltage characteristics of the cell



where the oxygen partial pressure established by the Ni, NiO and Cu, Cu<sub>2</sub>O electrodes was  $8 \times 10^{-30}$  and  $2 \times 10^{-19}$  atm, respectively.

## 5. Discussion

As seen from table 1, all the compositions studied here initially formed a continuous series of solid solutions of the  $\gamma_{\text{II}}\text{-Li}_3\text{PO}_4$  type. Therefore, the initial conductivity measurements were all done on materials with the same structure.

The admittance response shown in fig. 2 is very similar to that reported by von Alpen et al. [2] for lisicon, who attributed the response to a mixture of bulk ionic and intergranular impedance, i.e. a grain-boundary-transfer resistance. These phenomena are modelled by the series combination of resistance elements in the equivalent circuit of fig. 2. The limited frequency range available precluded a direct measure of the bulk ionic conductivity. At 50°C the bulk ionic conductivity of lisicon, extracted from fitting the circuit elements of fig. 2 to the experimental data, is seen in fig. 3 to be even slightly higher than that of von Alpen et al. [2]. Von Alpen et al. [2] reported that above about 200°C the semicircle due to the grain-boundary-transfer resistance disappears, meaning that this resistance element is negligible in comparison with the bulk ionic resistance, so presumably for  $T > 200^\circ\text{C}$  the bulk ionic conductivity is measured. The conductivity data of lisicon reported here, and by von Alpen et al. [2], are both lower than those of Hong [1].

The geometric capacitances found by circuit fitting were of the order of 5 pF, which is the expected order of magnitude. The equivalent circuit of fig. 2 only models the high-frequency response, and for low frequencies an additional interfacial capacitance must be added in series with the entire circuit to account for the ionically blocking Pt electrodes.

Since the sample conductance data shown in fig. 4 are a combination of the bulk ionic and grain-boundary-transfer resistances, they can be taken as the minimum value for the bulk ionic conductivity. Therefore, since the bulk ionic conductivity of lisicon is lower than the sample conductance of compositions 3, 4, 5, 7, 8, and 10, these compositions have a higher bulk ionic conductivity than lisicon. Compositions 7, 8 and possibly 5 have higher bulk ionic conductivities than their counterparts in the Li<sub>4</sub>SiO<sub>4</sub>-Li<sub>3</sub>PO<sub>4</sub> system.

Since in most instances only the combination of bulk ionic and grain-boundary-



transfer resistances could be measured, a detailed interpretation of the conductivity differences between these solid solutions is not justified. The Li ionic conductivity increased with the substitution of  $\text{P}^{5+}$  for  $\text{Ge}^{4+}$ , both for compositions with a constant mobile Li content, compositions 1  $\rightarrow$  9  $\rightarrow$  8, and also for those with a decreasing mobile Li content, i.e. constant total Li content, compositions 1  $\rightarrow$  4. This indicates that the conductivity is not strongly affected by the number of mobile Li, but that their mobility is greatly increased by slight structural changes caused by the  $\text{P}^{5+}$  [17].

Water has been shown to influence the ionic conductivity of some Li compounds [18,19] leading to a large increase in the conductivity at  $\approx 400^\circ\text{C}$ . This is attributed to a layer of LiOH which forms at the grain boundaries due to a reaction with water, and an increase in the ionic conductivity of this LiOH layer at  $\approx 400^\circ\text{C}$ . Since no step increase in the conductivity at  $\approx 400^\circ\text{C}$  was observed for the solid solutions reported here, there seems to be no significant contribution to the conductivity from a LiOH layer. Bayard [20] has recently reported that in lisicon, the grain-boundary-transfer resistance was affected by the presence of water, while the bulk ionic conductivity remained unchanged.

West and Glasser [12] reported that for  $\text{Li}_3\text{PO}_4$  where the  $\gamma_{\text{II}}$ -form was quenched in, the  $\gamma_{\text{II}} \rightarrow \beta_{\text{II}}$  transformation was observed only in the presence of water or water vapor.

From table 1 it is seen that after the conductivity measurements, in which the samples were at temperatures above  $350^\circ\text{C}$  for 4–16 h, the low  $\text{Li}_4\text{GeO}_4$  phase was present for some compositions. The irreversible conductivity decrease at elevated temperature is thus attributed to the formation of the low conductivity low  $\text{Li}_4\text{GeO}_4$  phase on decomposition of the solid solution. Lisicon is thus seen to be structurally metastable at low temperatures, decomposing to two phases at a measurable rate, as evidenced by the decrease in conductivity, at  $T > 350^\circ\text{C}$ . Compositions 2, 3, 4, and 9 also appear to be structurally metastable. No determination was made of the temperature range in which the initial  $\gamma_{\text{II}}$ -type solid solutions are stable. The conductivity and structure of composition 10 did not change on heating. By comparison with the  $\text{Li}_4\text{SiO}_4\text{-Li}_2\text{ZnSiO}_4$  system [13], this suggests that composition 10 is within a one-phase region. That no conductivity decrease was observed for samples in the  $\text{Li}_4\text{GeO}_4\text{-Li}_3\text{PO}_4$  system is taken to indicate that there is no structural decomposition or  $\gamma \rightarrow \beta$  transition in these solid solutions, the same behavior as in the analogous  $\text{Li}_4\text{SiO}_4\text{-Li}_3\text{PO}_4$  system.

It is suggested that von Alpen et al. [2] did not observe this decrease in conductivity due to the structural decomposition, since with their fully automated ac conductivity measuring system [21] they were able to rapidly measure over the entire temperature range avoiding the extended periods at a given temperature (overnight) encountered in manual measurements. In their dc measurements, which were all made at  $T < 300^\circ\text{C}$ , the decomposition was probably not observed because of the sluggish transformation kinetics.

The electronic conductivities in these solid solutions are very low. The slight in-

crease of electronic conductivity with increasing oxygen partial pressure suggests the incorporation of oxygen by a mechanism such as



leading to p-type conductivity. It is, however, apparent that under low oxygen partial pressure conditions, i.e. the N<sub>2</sub> ambient and with the Cu, Cu<sub>2</sub>O and Ni, NiO electrodes, the conductivity is essentially entirely ionic.

## 6. Conclusions

In the system Li<sub>4</sub>GeO<sub>4</sub>-Li<sub>2</sub>ZnGeO<sub>4</sub>-Li<sub>3</sub>PO<sub>4</sub> a wide range of solid solutions form with the  $\gamma_{\text{II}}$ -type structure. Several of these solid solutions have higher bulk ionic conductivities than lisicon, which was reported to be the best Li solid electrolyte to date in the temperature range 300-400°C. However, it was found that certain of these solid solutions are structurally metastable at low temperatures, but only decompose forming low Li<sub>4</sub>GeO<sub>4</sub> at a measurable rate at  $T > 350^\circ\text{C}$ . This structural decomposition leads to an irreversible decrease in conductivity. Clearly a phase study of the Li<sub>4</sub>GeO<sub>4</sub>-Li<sub>2</sub>DGeO<sub>4</sub>, D = Zn, Mg, is needed to identify the one-phase regions.

Since lisicon was found to be thermodynamically unstable against Li, emphasis should be placed on the Li<sub>4</sub>SiO<sub>4</sub>-Li<sub>2</sub>MgSiO<sub>4</sub> system which is expected to be the most thermodynamically stable against Li of the systems studied by Hong [1].

Along the Li<sub>4</sub>GeO<sub>4</sub>-Li<sub>3</sub>PO<sub>4</sub> tie line, solid solutions form which do not structurally decompose, or undergo a phase transformation. The bulk ionic conductivity at 200°C in these solid solutions is higher than in lisicon, and also in the corresponding solid solutions in the Li<sub>4</sub>SiO<sub>4</sub>-Li<sub>3</sub>PO<sub>4</sub> system.

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