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Ionic Conductivity of LISICON Solid Solutions, $Li_{2+2x}Zn_{1-x}GeO_4$

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The conductivity of LISICON γ_{II}-type solid solutions of general formula $Li_{2+2x}Zn_{1-x}GeO_4$ ($-0.36 < x < 0.87$), which are members of a promising new class of Li^+ ion conductors, was measured over the temperature range ~25 to 300°C. Conductivities appear to be very composition dependent near the stoichiometric composition $x = 0$, but less so in the range $0.15 \leq x \leq 0.87$. It is shown that interstitial Li^+ ions rather than cation vacancies give rise to high conductivities. The solid electrolyte properties and possible applications of the solid solutions are evaluated. The LISICON composition, $x = 0.75$, decomposes readily above ~300°C by precipitation of Li_4GeO_4, thereby limiting its possible usefulness, but compositions in the range $x = 0.45$ to 0.55 appear to be stable at all temperatures. However, irreversible decreases in conductivity (aging effects) occur on annealing, even at room temperature. The conductivity data of quenched samples give linear Arrhenius plots, but with anomalously high prefactors, over the range ~25 to 130°C; at higher temperatures reversible changes of slope to lower activation energies occur. A variety of minor polymorphic transitions occur on annealing γ_{II} solid solutions below ~300°C and their relationship to the conductivity was also determined.

Introduction

LISICON, $Li_{14}Zn(GeO_4)_4$, is one member of a wide range of solid solutions of formula, $Li_{2+2x}Zn_{1-x}GeO_4$ ($-0.36 < x < 0.87$) (*1*). It has been reported to possess an ionic conductivity at 300°C of 0.13 ohm^{-1} cm^{-1}, which is the highest conductivity for any Li^+ ion conductor at this temperature (*2*). The solid solutions are based on stoichiometric γ_{II} Li_2ZnGeO_4, which is isostructural with γ_{II} Li_3PO_4 (*1, 3*) and is derived by the double substitution mechanism

$$P^{5+} \rightarrow Ge^{4+},$$

$$Li^+ \rightarrow Zn^{2+}.$$

The γ_{II} solid solutions in the system Li_4GeO_4–Zn_2GeO_4, of which LISICON is one member, form by the mechanism (*1, 4, 5*)

$$2Li^+ \leftrightarrow Zn^{2+}.$$

Thus the lithium-rich solid solutions, including LISICON, contain interstitial Li^+ ions which occupy distorted octahedral sites (*2, 4*), and the zinc-rich solid solutions contain vacant Li^+ tetrahedral sites (*1*).

The formula of the lithium-rich γ_{II} solid solutions may be written as

$$Li^{i}_{x}[Li_{2+x}Zn_{1-x}GeO_4]^{f},$$

in which x lithium ions occupy interstitial sites and all the other ions, given in square brackets, form a structural framework. Structure determinations of two different compositions have been reported: $x = 0.5$ (4) and $x = 0.75$ (2). Both give essentially the same positions for the framework ions. Within this framework, the Ge^{4+} ions are

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tetrahedrally coordinated; Li^+ and Zn^{2+} ions are also tetrahedral and are distributed in a disordered manner over 8(*d*) and 4(*c*) sites. The distribution is not completely random since in both structure determinations the Zn^{2+} ions show a small preference for the 8(*d*) sites. The MO_4 tetrahedra formed by the (Li^+, Zn^{2+}) framework ions share corners and some edges with each other but only corners with the GeO_4 tetrahedra, which are isolated from each other.

The two structure determinations differ somewhat in the positions occupied by the interstitial Li^+ ions. For $x = 0.50$ (*4*), these ions are in a set of 8(*d*) sites with 25% occupancy (the unit cell contains four formula units and therefore two interstitial Li^+ ions per cell for $x = 0.50$; this is consistent with an occupancy of 25% in eightfold sites); these sites are off-center positions in distorted octahedra and there are two such sites per octahedron although at any time only one of each may be occupied. It was suggested (*4*) that the occupancy of these 8(*d*) sites varies with and is governed by the solid solution composition.

For $x = 0.75$ (*2*), some of the interstitial Li^+ ions are placed slightly off-center in 4(*c*) sites with an occupancy of 55% and the remainder are placed in 4(*a*) sites with an occupancy of 16%. There appears to be a considerable discrepancy between the two structure determinations; however, on closer examination it is seen that the atomic coordinates of Li^+ in the 4(*c*) sites, $x = 0.75$ (*2*), and in the 8(*d*) sites, $x = 0.50$ (*4*), are quite similar. This arises because each 4(*c*) site, which has a grossly distorted octahedral environment, is split into two sites in the 8(*d*) set used in Ref. (*4*). Therefore, the two determinations appear to be in fairly good agreement over the partial occupancy of these sites.

The main difference in the two structure determinations concerns the 4(*a*) sites in Ref. (*2*). If these sites are occupied in $x = 0.75$, this would imply a change in solid solution mechanism occurring at $x \sim 0.5$; i.e., Li^+ ions would begin to enter 4(*a*) sites for $x \gtrsim 0.5$. It is possible, however, that this result is incorrect because (a) a Li^+ ion in a tetrahedral 4(*a*) site would share faces with two adjacent GeO_4 tetrahedra, which appears unlikely from electrostatic repulsion considerations, and (b) the isotropic temperature factor, β_0 (Ref. (*2*), Table 1), for these 4(*a*) Li^+ ions is very high. While such a high β_0 value may indicate that the Li^+ ions are mobile, it could also indicate that this site is, in fact, empty. No such anomalous β_0 exists for 8(*d*) sites (*4*).

In conclusion, therefore, there is still some uncertainty over the positions of the interstitial Li^+ ions. A possible complication in structure determinations on these solid solutions is that they exhibit polymorphism. From the results of annealing at low temperatures, it has been suggested that a family of "low γ phases" may exist (*1*) and evidence is presented for the occurrence of yet more of these γ derivative phases. These polymorphs may be associated with ordering of the Li^+ ions, as has been found to occur in Li_4SiO_4 (*6*).

Within the framework of the solid solutions, there are a large number of interstitial sites which, according to Hong (*2*), link up to form two-dimensional conduction pathways for the interstitial Li^+ ions. The details of the conduction mechanism are not clear. A simple hopping mechanism for Li^+ ions is possible, but alternative mechanisms, including various interstitialcy mechanisms, can also be formulated.

The conductivity of LISICON solid solutions is entirely due to Li^+ ions. Four-probe dc ionic conductivity and dc ionic polarization measurements showed that the transport number of Li^+ ions is essentially unity (*7*). Alternating current measurements suggested the presence of grain boundary effects in polycrystalline samples (*7–10*). Although several studies of the conductivity of LISICON, $x = 0.75$, have been reported, there is considerable disagreement between the values. Both Hong (*2*) and Bayard (*8*) reported values at 300°C which are about one order of magnitude larger than those found by von Alpen *et al.* (*7*). In addition, various deviations from linearity in the Arrhenius plots have been observed (*2, 5, 7, 8*). Kamphorst and Hellstrom (*5*) found that LISICON, $x = 0.75$, is metastable at room temperature and that, on annealing at elevated temperatures, ≳350°C, precipitation of Li_4GeO_4 occurs, accompanied by an irreversible decrease in the conductivity. In considering the possible applications of LISICON as the solid electrolyte in novel batteries, it has been found that it reacts violently with molten Li at 200°C, thereby limiting its possible usefulness (*7*).

The phase diagram of the γ_{II}, LISICON-containing system Li_4GeO_4–Zn_2GeO_4 has been determined (*1*): it is reproduced in Fig. 1. The thermodynamic metastability of LISICON, $x = 0.75$, was confirmed but it was found that a small range of more zinc-rich compositions, around $x = 0.5$, appears to be stable at all temperatures. These compositions may therefore be of more use than LISICON as a practical, high-temperature solid electrolyte. In this paper, the conductivity of various compositions in the range $-0.3 < x < 0.87$ has been measured and the results correlated with composition, polymorphism, and aging of the γ_{II} solid solutions.

Conductivity in the γ_{II}-type solid solutions is also of interest from a theoretical standpoint because it is one of the few solid electrolyte systems which exhibits such a wide range of concentration of mobile species within a relatively well-characterized solid solution system, together with a changeover from a Li^+ interstitial to a Li^+ vacancy solid solution mechanism at the composition Li_2ZnGeO_4. Li_2ZnGeO_4 is just one member of a large family of compounds which possess a γ tetrahedral structure (*1*). Many of these are capable of forming interstitial solid solutions with Li_4XO_4 compounds (X = Si, Ge) resulting in a high Li^+ ion conductivity (*11, 12*). Few systematic studies on this important class of solid electrolytes have, as yet, been made.

In the first stage of this work (*10*), a detailed study of the ac response of polycrystalline pellets of LISICON, γ_{II} solid solutions was made. It was found that significant grain boundary resistances were always present and that these were associated with constriction of the current pathways at the areas of contact between

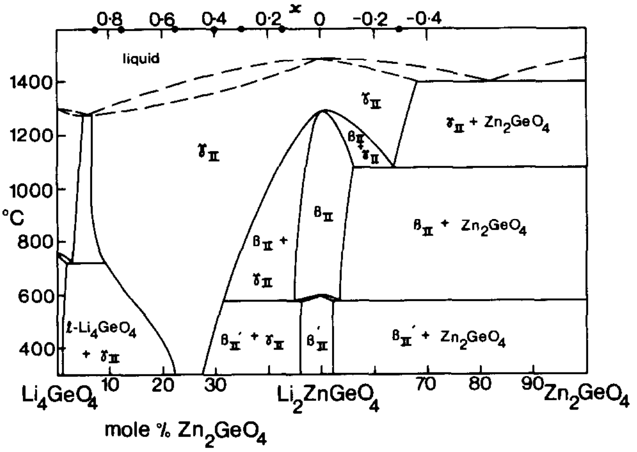

FIG. 1. Phase diagram of the system Li_4GeO_4–Zn_2GeO_4 (*1*). The upper abcissa gives the composition (x) of the γ_{II} solid solutions, $Li_{2+2x}Zn_{1-x}GeO_4$; compositions studied are marked by solid circles.

grains. A characteristic feature of the constriction resistances was that, for a given pellet, the activation energy associated with the temperature dependence of the constriction resistance was almost always the same as the activation energy associated with the intragranular (bulk) resistance. Attempts were made to model the ac response of the pellets using equivalent electrical circuits and it was found to be necessary to introduce a frequency-dependent admittance, or Jonscher element, into both the intragranular and grain boundary circuit simulations (*10*).

Experimental

Details of sample preparation by solid-state reaction and analysis by X-ray diffraction and DTA have been given earlier (*1*). Pellets were prepared by cold-pressing powders of the γ_{II}-type solid solutions at 45,000 psi followed by sintering at temperatures between 1000 and 1100°C for 1½ to 2 hr. A few pellets were covered with powder of the same composition (to reduce lithia loss) and sintered at 1200°C for 5 to 10 hr. Pellet densities were typically 75 to 80% of the theoretical values.

Gold electrodes were applied to opposite pellet faces by either evaporation or pasting. Measurements were carried out in vacuum, N_2, and air, temperatures being controlled and measured to ±1°C. Conductivities were measured by ac techniques and the data were analyzed by complex impedance, admittance, and electric modulus formalisms (*10*). Analysis of the data was

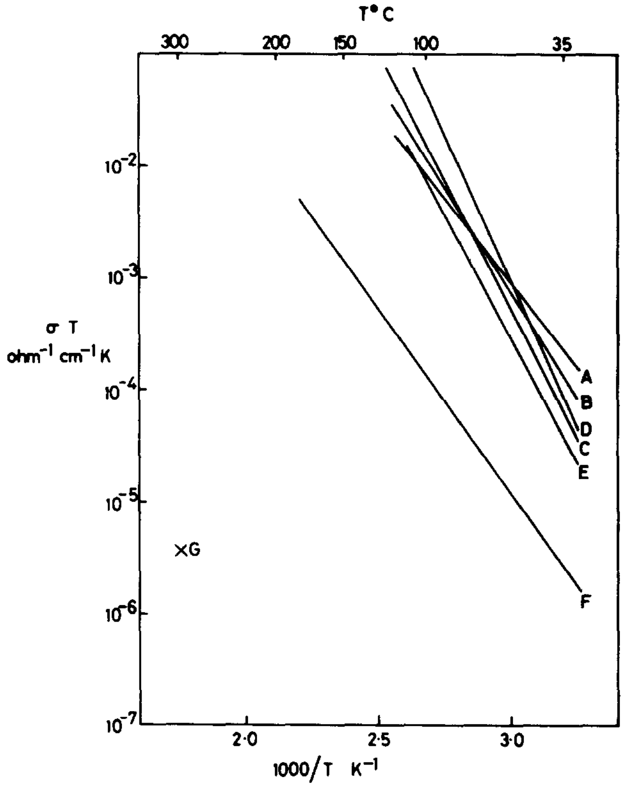

FIG. 2. Intracrystalline (bulk) conductivity of $Li_{2+2x}Zn_{1-x}GeO_4$ solid solutions. x values are *A* (0.85), *B* (0.75), *C* (0.55), *D* (0.40), *E* (0.30), *F* (0.15), and *G* (−0.30).

complicated because of the presence of an intergranular resistance and is described separately, together with details of the equipment used (*10*).

Results and Discussion

General Comments

The conductivity of pellets of seven different compositions was measured; these were $Li_{2+2x}Zn_{1-x}GeO_4$: $x = 0.85, 0.75, 0.55, 0.40, 0.30, 0.15$, and -0.30. Homogeneous γ_{II} ($x = 0.85$ to 0.30) or closely related γ_{II} derivative ($x = 0.15, -0.30$) solid solutions were initially prepared by quenching samples from ~1000 to 1200°C. As can be seen from the phase diagram, Fig. 1, all the compositions studied form stable γ_{II} solid solutions at these high temperatures but below ~400°C, only compositions $x = 0.55$ and 0.40 are stable as γ_{II} solid solutions. For most other compositions, however, once the γ_{II} solid solutions had been quenched to room temperature, they were kinetically stable and could be safely heated to ~300°C before any decomposition of the γ_{II} structure occurred by, e.g., precipitation of Li_4GeO_4, γ_{II} Li_2ZnGeO_4, or Zn_2GeO_4, depending on composition.

The conductivity results are presented as Arrhenius plots of log σT against T^{-1} in Figs. 2 and 3. Data in Fig. 2 are limited to the temperature range 25 to 130°C (apart from point G) and correspond to bulk, intracrystalline conductivities. At higher temperatures it was not possible, with the equipment available, to separate inter- and intragranular conductivities and the data in Fig. 3, which cover a wider temperature range, represent net pellet conductivities. The intergranular resistances appear to be associated with constriction of the conduction pathways (*10*) and, as found in the

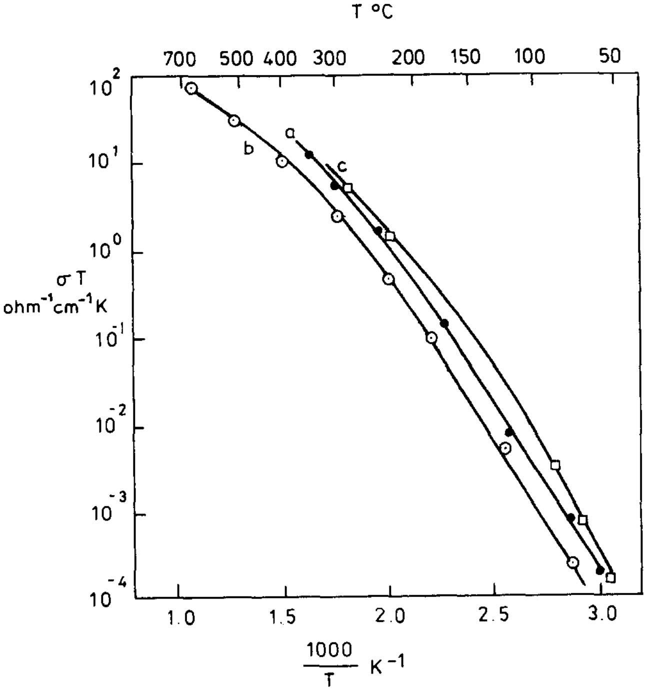

FIG. 3. Total conductivities (intracrystalline + grain boundary) of $Li_{2+2x}Zn_{1-x}GeO_4$ solid solutions: x values are (*a*) 0.75, (*b*) 0.55, and (*c*) 0.40.

range 25–130°C, the Arrhenius plots of the overall conductivity are parallel to those for the bulk conductivity but are reduced by a factor of 2 to 8.

It was found that the bulk conductivity data below 130° and for $x > 0$ were consistent and reproducible for quenched samples. At higher temperatures, however, the overall pellet conductivities were less well behaved, for three reasons: (i) the Arrhenius plots showed a reversible change in slope, Fig. 3; (ii) irreversible decreases in conductivity occurred on annealing for protracted times without any corresponding changes in the X-ray powder pattern (such effects also occurred <130°C), and (iii) various polymorphic transitions occurred; some affected the conductivity but many did not. Three compositions—$x = 0.40, 0.55, 0.75$—were studied in some detail in order to investigate these various effects.

The remainder of this paper deals in turn with:

1. General relationships between conductivity and composition.
2. Trends in the bulk conductivity of interstitial solid solutions for $x = 0.15$ to 0.85.
3. Reversible change of slope in the Arrhenius plots at high temperature.
4. Irreversible decreases in conductivity (aging effects) over the entire temperature range studied.
5. Polymorphism of γ_{II} solid solutions and its relationship to conductivity.

1. Relationships between Conductivity and Composition

(a) Zinc-rich solid solutions. The composition $x = -0.30$ was the only one studied which was on the zinc-rich side of the stoichiometric composition Li_2ZnGeO_4. The sample, prepared by quenching from ~1200°C, had a γ_{II} derivative structure. Only one data point could be obtained for this composition, at 300°C (Fig. 2). At lower temperatures, the conductivity was too low to be measured, i.e., $\lesssim 10^{-9}$ ohm^{-1} cm^{-1}, and at higher temperatures, the sample decomposed to give the equilibrium mixture of β_{II}–Li_2ZnGeO_4 and Zn_2GeO_4; similar results are anticipated for most of these vacancy γ_{II} solid solution compositions. Although the conductivity was measured at only one temperature, it can be seen from Fig. 2, point G, that it is several orders of magnitude lower than that of the lithium-rich, interstitial solid solutions. Since composition $x = -0.30$ contains Li^+ vacancies relative to stoichiometric Li_2ZnGeO_4, it is clear that vacancies do not lead to high conductivity in these γ_{II} solid solutions.

Unfortunately, it was not possible to make conductivity measurements on γ_{II}-type solid solutions close to the stoichiometric composition Li_2ZnGeO_4. In the range $-0.2 \lesssim x \lesssim 0.1$, the γ_{II} solid solutions could not be quenched to room temperature; transformation to the β'_{II} polymorph always occurred. Therefore, all remaining measurements were made on lithium-rich compositions, $x > 0$.

(b) Lithium-rich solid solutions. The lithium-rich solid solutions, $x > 0$, contain interstitial Li^+ ions, and from Fig. 2 these clearly have much higher conductivity than the vacancy, $x < 0$, solid solutions. Although there are no data for $x = 0$, it appears that the conductivity must increase dramatically at first as interstitial Li^+ ions are introduced into the structure. At higher concentrations of interstitial Li^+ ions, a considerable range of γ_{II} solid solution compositions, $x \sim 0.30$ to 0.85, has comparable, high conductivities and therefore potential applications as a solid electrolyte. However, since the original LISICON composition, $x = 0.75$, is thermodynamically metastable with respect to precipitation of Li_4GeO_4 below ~650°C and rapidly decomposes above 300°C, compositions centered around $x = 0.50$ would appear to be more useful: these have a similar high conductivity to LISICON at, e.g., 200°C and appear to be stable at all temperatures below the

melting transition. A limitation to the possible applications of these materials, however, is the occurrence of aging effects, which are discussed later.

2. Intracrystalline Conductivities of Lithium-Rich Solid Solutions

The intracrystalline (bulk) conductivity data for compositions $x > 0$, Fig. 2, fit an Arrhenius format, log σT vs T^{-1}, for temperatures in the range 25 to 130°C. There is some doubt over the data for $x = 0.15$, curve *F*, since the ac analysis suggested an ambiguous, complex equivalent circuit for this composition which made difficult the extraction of the true, intracrystalline conductivities. The data for curves *F* to *A* change in a systematic but most unusual manner with changing composition. The data may be divided into two groups, (i) for $0.15 \lesssim x \lesssim 0.40$, curves *F* to *D*, and (ii) for $0.55 \lesssim x \lesssim 0.85$, curves *C* to *A*. For (i) the Arrhenius plots extrapolate back to a nodal point at $\sim 3 \times 10^{-8}$ ohm^{-1} cm^{-1} K and 260K. For (ii) the plots pass through a nodal point at $\sim 3 \times 10^{-3}$ ohm^{-1} cm^{-1} and 351K. A consideration of the Arrhenius equation and especially the magnitude of the prefactor for these low-temperature plots shows that the data cannot be explained by a simple hopping model of freely mobile interstitial Li^+ ions: the prefactor varies with composition by several orders of magnitude and, for most compositions, is much too high to be explained by such a model. An explanation in terms of defect interactions can account for the behavior and will be discussed subsequently (*13*).

3. Nonlinear Arrhenius Behavior

The higher-temperature ($\gtrsim$130°C) behavior is rather more complex and departures from Arrhenius behavior occur. The problem was complicated somewhat because intracrystalline conductivities, free from constriction effects, could not be obtained but this does not affect the general conclusions. The data for quenched γ_{II} solid solutions, $x = 0.55$ in Fig. 3, show a change in slope above ~180°C which was fully reversible on cooling. This change may be associated with a phase transition and/or with a change in conduction mechanism as discussed in Ref. (*13*). A similar change in slope was observed in composition $x = 0.40$.

4. Aging Effects

In this section, results are presented of irreversible decreases in conductivity with time (aging effects) which do not appear to be matched by changes in the X-ray powder patterns; such aging effects have been observed in interstitial solid solutions up to at least 300°C. The effects were most studied for composition $x = 0.55$ and are shown in Fig. 4. Curve *A* is for a freshly prepared pellet; curve *B* is for a similar pellet which was stored in vacuum at room temperature for 28 days prior to making the conductivity measurements. The room-temperature conductivity of the aged sample was almost 100 times less than that of the fresh sample but the difference in conductivity decreased with increasing temperature since the aged sample had a slightly higher activation energy; the prefactor was also slightly higher in aged samples. From an analysis of the ac data (*10*), the aging was shown to be due to a true, intracrystalline effect and not due to changes in the equivalent electrical circuit of the pellets, such as would be associated with the creation of large grain boundary resistances. Thus, because the overall pellet resistance was already a combination of the crystal resistance and the constriction resistance due to the small area of contact between the grains, both of these resistances increased to the same degree on aging.

Very few apparent changes in the X-ray powder pattern of the γ_{II} phase occurred on aging. The only change was a possible broadening of the 020 line at 3.13 Å in the aged samples of this composition. It is pos-

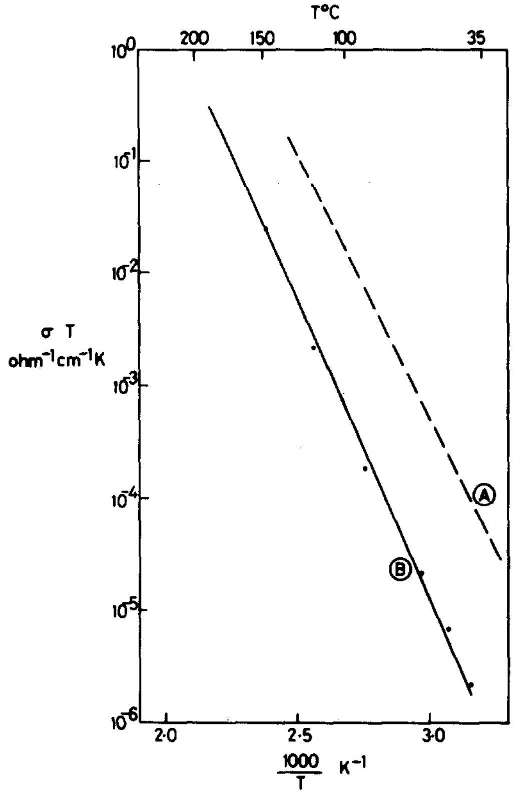

FIG. 4. Intracrystalline conductivity of freshly prepared (*A*) and aged pellet (*B*) of composition $x = 0.55$. Aging treatment: 28 days in vacuum at 25°C.

sible, of course, that long-range structural changes (polymorphism) occurred which did not show up by powder diffraction and these may be detected by single-crystal diffraction methods.

Aging effects in other compositions were observed at higher temperatures but have been less well studied. Always an irreversible decrease in conductivity occurred with time. One possible example of this is the irreversible decrease in conductivity above ~200°C for solid solutions of composition $x = 0.75$ (Fig. 3(*a*)). This was not associated with precipitation of a poorly conducting phase but it may possibly be associated with the formation of the γ_{II} polymorph, γ_{II}'''.

The cause of the aging appears to be closely connected with the mechanism of conduction and can be accounted for by invoking a model involving the clustering of defects (*13*). Such clusters should be detectable by diffuse scattering methods.

Aging effects which occur, even at room temperature, are a serious drawback to the possible applications of the present solid electrolytes.

5. *Dependence of Conductivity on Polymorphism*

The γ_{II} solid solutions exhibit a large number of phase transitions on annealing at low temperatures, ≤300°C, for times ranging from several hours to a few weeks. Some of these transitions lead to a small but significant reduction in conductivity and others have little or no effect on conductivity. Of the compositions studied, the most distinctive polymorphism is exhibited by $x = 0.75$; this composition is discussed in detail with additional comments on $x = 0.40$ and a polymorph, "low γ," that appears to be common to most compositions.

(*i*) *LISICON composition, x = 0.75*. This composition shows complex polymorphism on annealing in the temperature range ~100 to 300°C. Three different variants on the γ_{II} structure were identified and labeled γ_{II}', γ_{II}'', and γ_{II}'''; all were obtained at room temperature. Their X-ray powder diffraction patterns, recorded with a Guinier focusing camera, are shown as schematic line diagrams in Fig. 5. They differ from the parent γ_{II} pattern in that some lines in γ_{II} split into doublets in the derivative phases and/or extra lines appear. The following sequences are typical of the transformations which could be effected:

$$\gamma_{II} \xrightarrow[\text{vacuum, 100°C}]{\text{6–8 hr, in}} \gamma_{II}' \xrightarrow[\text{200°C}]{\frac{1}{2}\text{ hr}} \gamma_{II}, \tag{1}$$

$$\gamma_{II} \xrightarrow[\text{160 to 270°C}]{\text{12 hr, in vacuum}} \gamma_{II}'' \xrightarrow[\text{280°C}]{\text{2 hr}} \gamma_{II}''', \tag{2}$$

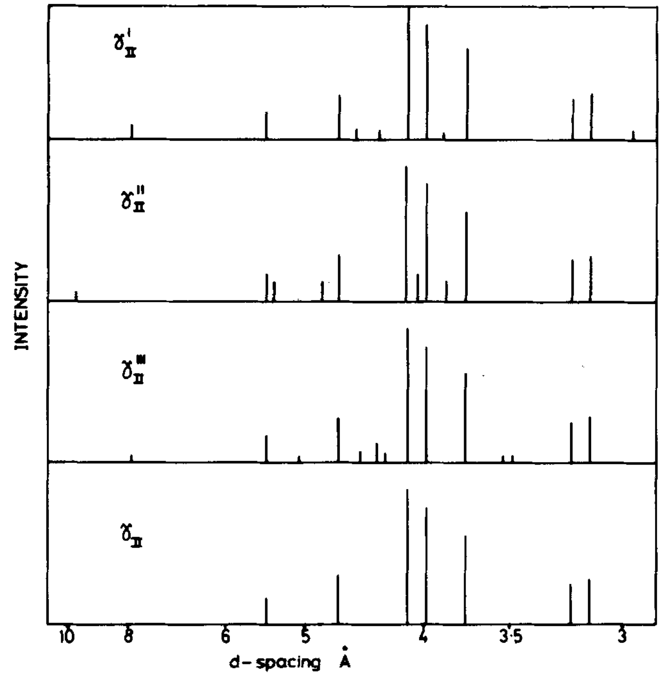

FIG. 5. X-Ray powder diffraction line diagrams of some γ_{II}-type phases for $x = 0.75$. Data taken from Guinier films.

$$\gamma_{II} \xrightarrow[300°\text{C}]{12\text{ hr, in vacuum}} \begin{array}{l}\text{precipitation of } Li_4GeO_4 \text{ from} \\ \quad\text{supersaturated } \gamma_{II} \\ \quad\text{solid solutions}\end{array} \quad (3)$$

A DTA trace of a quenched, single-phase γ_{II} sample is shown in Fig. 6a. A small exotherm is observed at 141°C followed by an endotherm at 189°C. These peaks are attributed to the sequence of changes

$$\gamma_{II} \xrightarrow[141°]{} \gamma'_{II} \xrightarrow[189°]{} \gamma_{II}.$$

The exothermic nature of the peak at 141°C indicates that the γ'_{II} phase is more stable (i.e., has lower ΔH) than γ_{II}, not only in the range 141 to 189°C but also below 141°C. These DTA effects correlate with reaction scheme (1) which was observed from the X-ray results of annealing experiments. There was no evidence for the $\gamma_{II} \rightarrow \gamma''_{II}$ transformation, reaction scheme (2), on DTA, probably because the times needed to form γ''_{II} were too long for the reactions to occur during the DTA cycle. An additional small endotherm appeared at ~280°C, not shown in

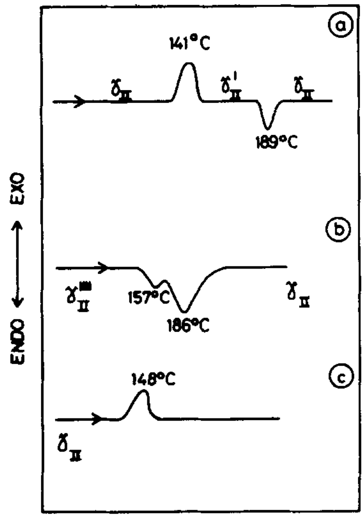

FIG. 6. DTA traces of some γ_{II}-type phases; (a) $x = 0.75$, (b) $x = 0.40$, (c) $x = 0.40$.

Fig. 6a, and is probably attributable to the transition $\gamma_{\mathrm{II}} \rightarrow \gamma_{\mathrm{II}}'''$. No heat effects attributable to the precipitation of Li_4GeO_4, reaction scheme (3), were observed up to 300°C.

The structures of the γ_{II}', γ_{II}'', and γ_{II}''' polymorphs are not known but they are possibly formed by ordering of the γ_{II} structure. For instance, the γ_{II}' X-ray powder pattern is similar to the γ_{II} pattern but contains a few extra lines, especially at low angles.

The effect of these various polymorphic transitions on the conductivity is shown in Fig. 7. After each data point was obtained, the cell was removed from the furnace and cooled in vacuum and a small amount of the pellet scraped off for X-ray diffraction. The results show that, apart from the normal effects of temperature on conductivity, the conductivity is insensitive to the sequence of changes $\gamma_{\mathrm{II}} \rightarrow \gamma_{\mathrm{II}}' \rightarrow \gamma_{\mathrm{II}}''$.

Above ~200°C, the conductivity shows an irreversible, downward departure from the straight line observed at low temperatures; this behavior is discussed in Section 4.

(*ii*) *Composition $x = 0.40$.* This composition possesses another γ_{II} derivative structure, γ_{II}''''; its X-ray powder pattern is similar to that of γ_{II} but with several lines broadened, notably 210 at 4.14 Å, 011 at 3.98 Å, and 002 at 2.58 Å. The DTA trace of γ_{II}'''' is quite distinct from that of γ_{II} (Figs. 6b and c). A sample of γ_{II}'''', prepared by annealing the γ_{II} polymorph overnight at 85°C in air, gave endotherms on DTA at 157

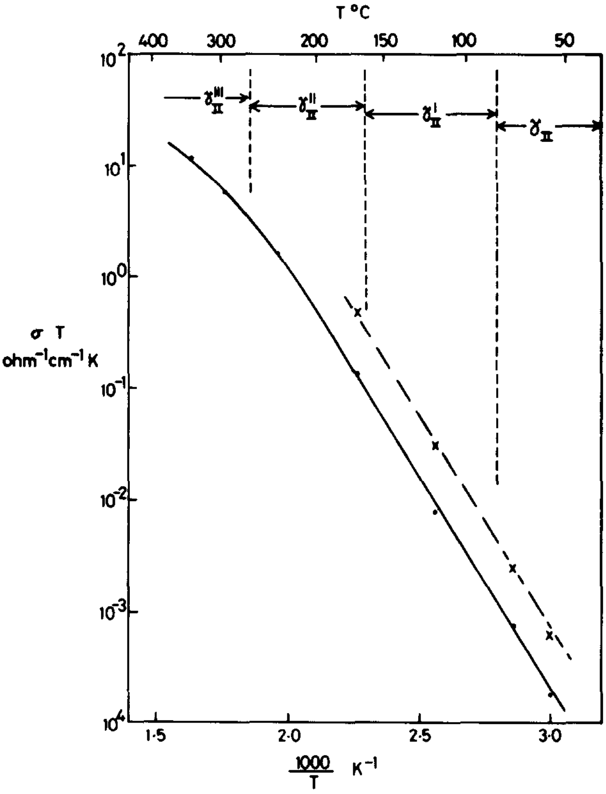

FIG. 7. Relationship between conductivity and polymorphism of γ_{II}-type solid solutions, $x = 0.75$. ●, total conductivity; ×, intracrystalline conductivity.

and 186°C (Fig. 6b), whereas a quenched γ_{II} sample gave a single exotherm at 148°C (Fig. 6c); therefore it appears from the DTA trace that other, unidentified, polymorphs exist for this composition.

(*iii*) *The "low-γ" polymorph.* On annealing γ_{II} solid solutions below 150°C, many compositions transform to a "low-γ" form (*1*). This is characterized by the doubling of certain lines in the X-ray powder pattern of γ_{II} and the magnitude of the splitting varies with composition. Formation of "low-γ" phases causes a drop in conductivity by a factor of 4 at room temperature.

In summary, the polymorphism of the γ_{II} solid solutions is clearly very complex and varies with composition. It appears likely that yet more polymorphs could be prepared under different conditions of annealing. Further work is needed in order to identify them and understand their relationship to conductivity.

Summary and Conclusions

Despite the complexity of behavior exhibited by the conductivities of γ_{II}-type solid solutions and the compositional constraints imposed by the low-temperature instability of γ_{II} solid solutions near the stoichiometric composition, it has been shown that stoichiometric γ_{II} Li_2ZnGeO_4 would probably have a very low conductivity and the introduction of large numbers of cation vacancies does not lead to a high conductivity. In the lithium-rich solid solutions, however, the interstitial Li^+ ions that are introduced result in a much higher conductivity.

For use as a solid electrolyte in practical devices, long-time stability is clearly necessary and for this reason compositions around $x = 0.5$, rather than the original LISICON composition $x = 0.75$, are likely to be more useful. However, aging effects, in which a large drop in conductivity occurs without any obvious, major structural change, are a serious drawback to the usefulness of these compositions. Such aging effects may be the cause of the considerable, unexplained variations in the reported conductivity of the LISICON, $x = 0.75$, composition (*2, 7–9*). Similar aging effects have been observed in a variety of other ionic conductors, such as oxide ion solid electrolytes (*14, 15*) and glasses, in which aging has been associated with structural relaxations that occur as a consequence of annealing (*16*); aging may be a common feature of many nonstoichiometric conductors (*13*).

The insensitivity of the conductivity to many of the polymorphic phase changes exhibited by the LISICON, γ_{II} solid solutions and the nature of the X-ray powder patterns of these polymorphs suggest that the polymorphism may be due in some way to an ordering of the framework Li^+ and Zn^{2+} ions, rather than involving the interstitial Li^+ ions.

An analysis of the prefactor and activation energy for the intracrystalline conductivity of the interstitial solid solutions indicates that a simple mechanism of conduction, in which all Li^+ ions can potentially participate, is not operative. Instead, a theory involving the interaction of defects is more appropriate; this theory, which is discussed elsewhere (*13*), can also account qualitatively for the curvature in the Arrhenius plots at high temperatures ($\gtrsim$200°C) and for the aging effects.

Further understanding of ionic conduction in the LISICON, γ_{II} solid solutions would be greatly assisted by the availability of single crystals for a range of compositions. It would then be possible to measure intracrystalline conductivities to much higher temperatures and also to assess the degree of anisotropy in the conductivity; since the γ_{II} solid solutions are orthorhombic, some anisotropy is likely.

The LISICON system is only one member of a family of solid solutions with the γ_{II} structure (*1, 5, 11, 12*), some of which have higher conductivity than LISICON at e.g., 25°C (*12*). A detailed study of other members of this family of Li^+ solid electrolytes would be important in understanding the mechanism of ionic conduction and, in particular, would allow an assessment of the importance of parameters such as bottleneck size, polarizability of the structural framework, and defect interactions to be made.

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