

## Percolative ionic conduction in the $\text{LiAlSiO}_4$ glass-ceramic system\*

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The effect of crystallinity on the lithium ion conductivity in  $\text{LiAlSiO}_4$  glass and glass-ceramic solid electrolytes has been determined. The ionic conductivity is thermally activated with an activation energy and preexponential factor that change in a marked and nonsimple manner as the volume fraction of crystallinity changes. These results are explained by using a continuum percolation model (effective medium approximation) which assumes that ionic conduction in the glass-ceramic is almost entirely within the glass phase until the crystalline volume fraction rises above  $\sim 55\%$ . The  $\text{LiAlSiO}_4$  system would seem to be nearly ideal for application of percolation theory since the crystalline phase,  $\beta$  eucryptite, has nearly the same composition as the glass phase. Hence, as the crystallite volume fraction increases in the glass-ceramic, the residual glass composition and conductivity remain the same. This is the first application of percolation theory to ionic transport in glass-ceramics and excellent agreement is obtained between theory and experiments for the  $\text{LiAlSiO}_4$  system.

### I. INTRODUCTION

The electrical properties of  $\text{LiAlSiO}_4$  materials are of interest because these materials are being considered as possible lithium ion conducting, high-temperature, solid electrolytes.<sup>1</sup> These are also good materials for fundamental studies of ionic transport since they can be prepared as single crystals,<sup>2,3</sup> glass,<sup>1,4</sup> or glass-ceramics,<sup>1,4</sup> all with the same composition ( $\text{LiAlSiO}_4$ ). The single crystals exhibit the  $\beta$  eucryptite structure<sup>2,3</sup> and are quasi-one-dimensional conductors with lithium ions transported primarily in channels parallel to the  $c$  axis.<sup>5,6</sup> The glass and glass-ceramic materials are, however, three-dimensional conductors.<sup>1</sup> The glass-ceramic is produced by controlled devitrification of the glass and consists of  $\beta$  eucryptite crystals imbedded in a glass matrix.

Our previous studies of ionic conductivity in  $\text{LiAlSiO}_4$  materials have indicated a large decrease in the ionic conductivity when the glass is converted to a glass-ceramic.<sup>1</sup> Other investigators have observed similar changes in the ionic conductivities of glass-ceramics upon devitrification.<sup>7-10</sup> In studies of other glass-ceramics, the glass and crystalline phases generally had different compositions, and the changes in the ionic conductivity were qualitatively explained in terms of variations in the composition and resultant conductivity of the glass phase as the crystalline phase(s) precipitated. Generally, no quantitative measurements of the glass phase : crystalline phase ratios were reported and the relative contribution of the glass and crystalline phases to the conductivity were unknown. The  $\text{LiAlSiO}_4$  system differs from those previously studied in that the crystalline phase in the  $\text{LiAlSiO}_4$  glass-ceramic

is  $\beta$  eucryptite which has the same composition as the glass. Hence as the crystallinity increases in the glass-ceramic, the residual composition and conductivity of the glass phase should remain the same. In this paper we report quantitative measurements of both the ionic conductivity and the crystalline fraction in the glass-ceramics. These features of our experiment have allowed us to develop a model to explain the ionic conductivity in this system.

A large part of the theoretical work that is presently being done on solid electrolytes is primarily concerned with explaining ionic conductivity in single crystals<sup>11</sup> and glasses<sup>12</sup> from a microscopic, atomic viewpoint. In this paper, we present a macroscopic model which complements this viewpoint. Ours is a continuum percolation model which treats the composite, glass-ceramic system as a random, binary mixture of the glass and crystalline phases. The degree to which the assumptions of the percolation model are in accord with the detailed chemical, structural, and electrical properties of the glass-ceramics and the possible extension of the percolation model to other glass-ceramics are discussed.

### II. MATERIALS PREPARATION

The glasses used in this investigation ( $\text{LiAlSiO}_4$  and  $\text{LiAlSiO}_4 + 2.8\text{-mole}\% \text{TiO}_2$ ) were prepared from reagent grade  $\text{Li}_2\text{CO}_3$  and the required oxides. These chemicals were mixed thoroughly and then melted and stirred in Pt crucibles at  $1600^\circ\text{C}$  for 16–24 h. After melting, the glasses were quenched and then annealed at  $650^\circ\text{C}$  for 5–10 min to remove strain. X-ray powder diffraction photographs of the glasses, taken after they were annealed, revealed no crystalline structure. Differential

TABLE I. Heat treatments and percent crystallinity (mass %) for  $\text{LiAlSiO}_4$  glass-ceramics.

Heat treatment	Crystallinity (mass %)
925 °C-5 h, 965 °C-16 h	88 ± 7
925 °C-5 h, 960 °C-5 h	81 ± 7
650 °C-2 h, 1000 °C-5 min, 915 °C-1 h	78 ± 6
675 °C-3.5 h, 940 °C-5 min, 830 °C-1 h	74 ± 6
580 °C-24 h, 725 °C-3 h, 740 °C-1 h	66 ± 5
650 °C-2 h, 725 °C-1 h	60 ± 5
600 °C-32 h, 650 °C-2 h, 670 °C-1 h, 680 °C-1 h	42 ± 4
600 °C-16 h, 650 °C-2 h, 670 °C-2 h	13 ± 1
600 °C-16 h, 650 °C-2 h, 670 °C-1 h	6 ± 1

thermal analysis performed on the glass, which contained  $\text{TiO}_2$ , indicated a glass transition temperature of 650 °C and a crystallization exotherm at 770 °C. The  $\text{TiO}_2$  was added to the  $\text{LiAlSiO}_4$  glass as a nucleating agent to aid in the formation of the glass-ceramics. Attempts to crystallize  $\text{LiAlSiO}_4$  glass without the nucleating agent resulted in preferential surface crystallization and cracking of the samples. All the glass-ceramics of different crystalline fraction are listed in Table I. These materials were cooled slowly after crystallization at a rate of about 10 °C/min to avoid cracking due to thermal stress. Such stresses could be introduced by differences in the thermal expansion of the glass and the crystalline phases. The most pronounced cracking, which occurred while the samples were cooled, was observed in the materials of low crystallinity where the heat treatments were below 770 °C. Extended heat treatments at high temperature (>950 °C) resulted in chalklike samples which were porous and cracked. For these reasons, no attempt was made to measure samples with a crystalline fraction greater than 88%.

### III. STRUCTURAL PROPERTIES

X-ray diffraction analyses of all the  $\text{LiAlSiO}_4$  glass-ceramics used in this study indicated the presence of only one crystalline phase,  $\beta$  eucryptite. Powder diffraction patterns yielded lattice parameters identical to those for single crystals<sup>2,3</sup> of  $\beta$  eucryptite [ $a = 10.49(1)$ ;  $c = 11.18(1)$  Å]. Other glass-ceramics that we have studied with compositions that differ from  $\text{LiAlSiO}_4$  contain either different crystalline phases or  $\beta$  eucryptite with different lattice parameters. For example, a glass-ceramic with the composition  $\text{Li}_2\text{Al}_4\text{Si}_6\text{O}_{19}$  has the  $\beta$  eucryptite structure with lattice parameters [ $a = 10.38(1)$ ;  $c = 10.88(6)$  Å] that differ from those of stoichiometric  $\beta$  eucryptite, and glass-ceramics with the composition  $\text{Li}_6\text{Al}_2\text{Si}_4\text{O}_{14}$  contain both the

$\beta$  eucryptite ( $\text{LiAlSiO}_4$ ) and lithium orthosilicate ( $\text{Li}_4\text{SiO}_4$ ) crystalline phases. The absence of phases other than  $\beta$  eucryptite from our glass ceramics and the identity of the lattice parameters of stoichiometric  $\beta$  eucryptite ( $\text{LiAlSiO}_4$ ) with those of our glass-ceramics indicate that the composition of the glass and crystalline phases in our glass-ceramics should be the same.

The method used to determine the percent of  $\beta$  eucryptite in the glass-ceramics is similar to one previously reported.<sup>13</sup> A series of standards were prepared from  $\beta$  eucryptite single crystals and  $\text{LiAlSiO}_4$  glass. These were ground to pass through a 325-mesh screen (0.044-mm opening). Silicon powder (325-mesh) was added as an internal standard at a constant mass fraction of the glass and single-crystal sample. The intensities of the (111) x-ray diffraction peak of Si and the (202) peak of  $\beta$  eucryptite were determined by the use of a scintillation counter, pulse-height analyzer,  $\text{CuK}\alpha$  radiation, and a graphite monochromator. A linear analysis of the intensity ratio ( $I_\beta/I_{\text{Si}}$ ) vs the mass percent of  $\beta$  eucryptite yielded the following:

$$\mathfrak{M} = (14 \pm 1)(I_\beta/I_{\text{Si}}),$$

where  $\mathfrak{M}$  is the mass % of  $\beta$  eucryptite. The density of the glass which contains  $\text{TiO}_2$  is 2.45 g/cm<sup>3</sup> and the theoretical density of  $\beta$  eucryptite is 2.351 g/cm<sup>3</sup>. Since there is only a slight difference in the densities of the glass and the crystalline phases, the mass percent and volume percent are nearly identical and differ at most by only one percent. The mass percentages determined by the x-ray analyses for the glass-ceramics are presented in Table I.

Scanning and transmission electron micrographs were obtained for some of the glass-ceramics to determine structural characteristics. Samples were prepared for scanning electron microscopy by mechanically polishing and then etching the sample by using a 0.1M HF acid solution. Scanning electron micrographs were also taken of a sample that was fractured and not polished or etched. Samples for transmission electron microscopy were prepared by mechanically slicing a thin section and then a hole with very thin edges was produced by ion bombardment of the thin section. The scanning electron micrographs show areas where the glass has been preferentially etched away but do not give any useful information about the crystalline material. The transmission electron micrographs give information about grain size and the type of crystalline phases present (Fig. 1). The grain sizes ranged from 0.3  $\mu\text{m}$  for the 13% glass-ceramic to 1.2  $\mu\text{m}$  for the 81% glass-ceramic. In the 81% glass-ceramic, small (50–100 Å) crystallites of  $\text{TiO}_2$  were detected in

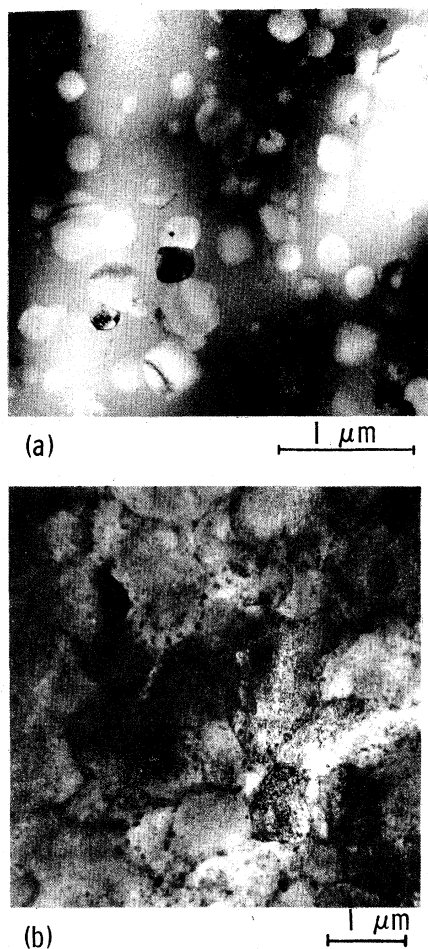


FIG. 1. Transmission electron micrographs of  $\text{LiAlSiO}_4$  glass-ceramics with 2.8-mole%  $\text{TiO}_2$  as a nucleating agent. (a) Micrograph of the 13% crystalline material with  $\sim 0.3\text{-}\mu\text{m}$  crystallites of  $\beta$  eucryptite; (b) micrograph of the 81% crystalline material with  $1.2\text{-}\mu\text{m}$  crystallites of  $\beta$  eucryptite. The small dark areas located primarily in the grain boundaries of the  $\beta$  eucryptite crystallites [in part (b)] are  $\sim 50\text{--}100\text{-}\text{\AA}$   $\text{TiO}_2$  crystallites.

the transmission electron micrographs and identified as  $\text{TiO}_2$  (rutile) by their electron diffraction patterns. (These were not observed in the x-ray diffraction patterns because of the size of the crystallites and/or their low concentration.) The  $\text{TiO}_2$  crystallites are concentrated in the  $\beta$  eucryptite grain boundaries [Fig. 1(b)]. From this observation, it can be concluded that at least part of the  $\text{TiO}_2$  is excluded from the  $\beta$  eucryptite as it crystallizes so that the glass-crystal boundary becomes enriched in  $\text{TiO}_2$ . This behavior has been observed in a previous study on the crystallization of glasses in the  $\text{Li}_2\text{O} + \text{Al}_2\text{O}_3 + \text{SiO}_2$  system which contained  $\text{TiO}_2$  as a nucleating agent.<sup>14</sup> That study

concluded that  $\text{Ti}^{4+}$  ions were preferentially located on the surface of  $\beta$  eucryptite crystals in the glass-ceramics that were investigated. The significance of the  $\text{TiO}_2$  enriched interface between the crystalline and glass regions is discussed in a later section.

#### IV. IONIC CONDUCTIVITY

##### A. Measurements

The samples used for the ionic conductivity measurements had dimensions of about  $1 \times 1 \times 0.1 \text{ cm}^3$ . Electrodes were applied by evaporating Cr onto the  $1 \times 1 \text{ cm}^2$  faces with the sample temperature at  $300\text{--}350^\circ\text{C}$ . The electrical measurements were made by using a three-terminal guarded ac technique.<sup>1</sup> In preparing samples for the guarded measurements, a circular groove was cut through the Cr contacts with sand-blasting techniques. This defined a center electrode area ( $\sim 0.35 \text{ cm}^2$ ) and an outer electrode area on each surface. The center circular electrodes were used for the conductance measurements. Electrical contact was made by using spring-loaded leads. The sample was connected to the measurement instrument by using two shielded coaxial cables. The leads to the outer electroded areas on the sample were connected to the grounded shields on the coaxial cables. For temperature-dependent conductivity measurements, thermocouples were bonded to the sides of the samples by using Omega CC high-temperature cement. The sample was supported by the spring-loaded leads between Ta strips which formed the heater arrangement. This assembly was mounted in a vacuum system, and measurements were made at  $\sim 10^{-6}$  Torr over the temperature range  $325\text{--}775 \text{ K}$ . The temperature gradient across the sample was  $1\text{--}2$  deg. The electrical measurements were made by using a Hewlett-Packard 4800A vector impedance meter with a 4810A direct measurement plug-in. With this instrument, measurements were made over the frequency range from 5 to  $5 \times 10^5 \text{ Hz}$ . The conductivity was determined from the conductance data in the frequency-independent region. In all of our impedance measurements, the phase angle was zero at some frequency in this region. This gave a direct measure of the real part of the impedance (i.e., the conductance) and thus gave assurance that the true sample conductance was being determined. Previous work has shown that the measured conductance (and thus the conductivity) is that associated with lithium ions in the bulk material.<sup>1</sup>

##### B. Results

Typical data obtained on the temperature dependence of the conductivity in the glass and glass-

ceramic materials for various degrees of crystallinity are shown in Fig. 2. These results show (i) that for the  $\text{LiAlSiO}_4$  glass (0% crystallinity) the  $\text{TiO}_2$  nucleating agent does not significantly affect the ionic conductivity (to the concentrations examined here, i.e., 2.8 mole%); (ii) that in the glass-ceramic, the conductivity generally decreases as the percent crystallinity is increased; and (iii) that  $\sigma$  varies exponentially with reciprocal temperature (i.e.,  $\sigma = \sigma_0 e^{-E/kT}$ ) over the temperature range examined.

Table II lists the conductivity activation energies  $E$  and preexponential factors  $\sigma_0$  for all the samples examined in these studies with different degrees of crystallinity. The  $E$  and  $\sigma_0$  values and their respective errors were determined from a least-squares analysis of the data. Plotting each of these experimental quantities separately against the crystallinity fraction (Figs. 3 and 4) emphasizes the fact that the conductivity is not changing in a simple average way. The results in Fig. 3 show that with increasing percent crystallinity, the value of  $E$  for the glass-ceramic is the same as that of the glass up to a value of ~55% crystallinity. As the degree of crystallinity increases beyond this point, the activation energy increases sharply and has a value of  $E \approx 1.23$  eV at 88% crystallinity. The  $\sigma_0$  values in Fig. 4 have a slightly different

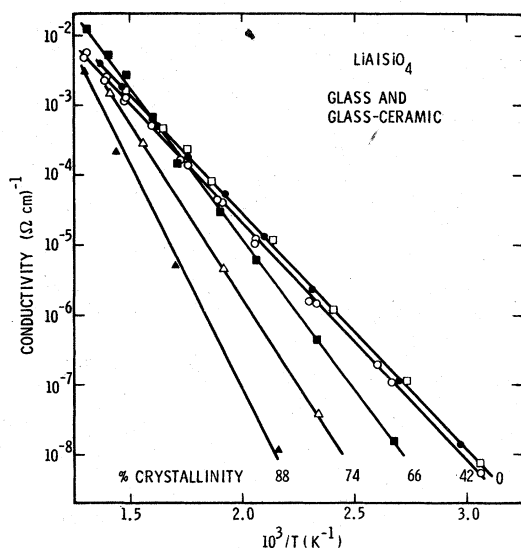


FIG. 2. Ionic conductivity temperature dependence of  $\text{LiAlSiO}_4$  glass and glass-ceramics with different degrees of crystallinity. For the glass (0% crystallinity), the  $\bullet$  data points are with no nucleating agent whereas  $\square$  denotes a glass with nucleating agent (2.8-mole %  $\text{TiO}_2$ ); there is no significant difference between these results. For the glass-ceramics the conductivity in the low-temperature region generally decreases with increasing percent crystallinity.

TABLE II. Ionic conductivity activation energies  $E$  and preexponential factors  $\sigma_0$  obtained from  $\sigma = \sigma_0 \exp(-E/kT)$  for  $\text{LiAlSiO}_4$  glass and glass-ceramics with varying degrees of crystallinity.<sup>a</sup>

Percent crystallinity	$E$ (eV)	$\sigma_0$ ( $\Omega \text{ cm}^{-1}$ )	
0 <sup>b</sup>	0.676 ± 0.003	$1.83 \times 10^2$	$\begin{pmatrix} +0.11 \\ -0.11 \end{pmatrix} \times 10^2$
6 ± 1	0.682 ± 0.004	$1.47 \times 10^2$	$\begin{pmatrix} +0.14 \\ -0.12 \end{pmatrix} \times 10^2$
42 ± 4	0.673 ± 0.005	$1.19 \times 10^2$	$\begin{pmatrix} +0.14 \\ -0.13 \end{pmatrix} \times 10^2$
60 ± 5	0.754 ± 0.010	$9.92 \times 10^2$	$\begin{pmatrix} +2.28 \\ -1.88 \end{pmatrix} \times 10^2$
66 ± 5	0.860 ± 0.011	$5.31 \times 10^3$	$\begin{pmatrix} +1.47 \\ -1.16 \end{pmatrix} \times 10^3$
74 ± 6	1.00 ± 0.011	$2.18 \times 10^4$	$\begin{pmatrix} +0.61 \\ -0.47 \end{pmatrix} \times 10^4$
78 ± 6	1.08 ± 0.014	$4.90 \times 10^4$	$\begin{pmatrix} +1.55 \\ -1.12 \end{pmatrix} \times 10^4$
81 ± 7	1.14 ± 0.035	$8.50 \times 10^4$	$\begin{pmatrix} +7.20 \\ -3.90 \end{pmatrix} \times 10^4$
88 ± 7	1.23 ± 0.047	$2.60 \times 10^5$	$\begin{pmatrix} +3.60 \\ -1.51 \end{pmatrix} \times 10^5$

<sup>a</sup> Conductivity data were analyzed using a least-squares method.

<sup>b</sup> Data on the glass are both with and without the  $\text{TiO}_2$  nucleating agent.

dependence on the degree of crystallinity. With increasing percent crystallinity  $\sigma_0$  first decreases and then dramatically increases as the percent crystallinity increases beyond the ~55% value. The critical value is the same for both the increase in  $E$  and the increase in  $\sigma_0$  with percent crystallinity, i.e., ~55% crystallinity. From these re-

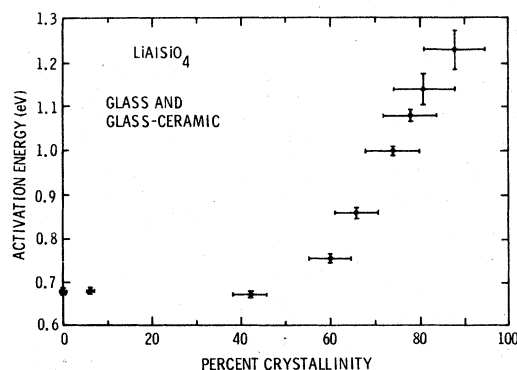


FIG. 3. Dependence of conductivity activation energy on percent crystallinity for  $\text{LiAlSiO}_4$  glass and glass-ceramic material.

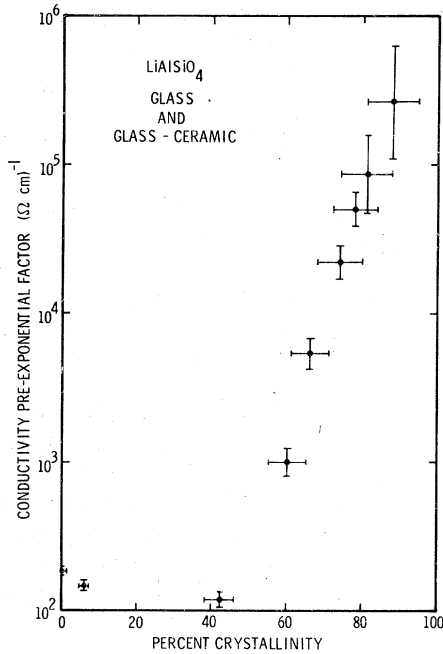


FIG. 4. Dependence of conductivity preexponential factor on percent crystallinity in  $\text{LiAlSi}_4$  glass and glass-ceramic material.

sults, it is obvious that the conductivity of these  $\text{LiAlSi}_4$  materials changes in a marked and non-simple manner as the volume fraction of crystallinity increases within the glass-ceramic material. While similar changes are often observed in other related glass-ceramics, this is the first study which presents a quantitative dependence of conductivity on crystallinity.

## V. DISCUSSION

### A. Material's properties

The  $\text{LiAlSi}_4$  glass-ceramic system would seem to be ideal for studying the effect of crystallinity on ionic conductivity, or in a more general context, the effect of random inclusions on glass ionic conductivity. Since the glass and the crystalline ( $\beta$  eucryptite) phases have nearly the same chemical composition and density,<sup>1</sup> the conductivity of each phase should remain constant as the degree of crystallinity changes. Hence the glass-ceramic conductivity ought to be describable simply as that of a binary mixture of two materials of different conductivities. Indeed, we propose a quantitative description of this type later in this section. However, there is a complication we wish to discuss beforehand. As the glass-ceramic becomes more crystalline, one might expect the activation energy and preexponential factor to have a trend towards pure, polycrystalline (ceramic)  $\beta$  eucryp-

tite. Experimentally, though, this is not observed. By using the data reported by Raistrick *et al.*<sup>15</sup> for the conductivity of hot-pressed, ceramic  $\beta$  eucryptite, one finds values of  $E \cong 0.9$  eV and  $\sigma_0 \cong 260$   $(\Omega \text{ cm})^{-1}$ . Neither of these values is close to the glass-ceramic endpoints indicated in Figs. 3 and 4 [i.e.,  $E \cong 1.2$  eV and  $\sigma_0 \cong 2 \times 10^5$   $(\Omega \text{ cm})^{-1}$ ]. Another measure of this discrepancy may be obtained from the experimental conductivity of single crystal  $\beta$  eucryptite. This crystal has a highly anisotropic, nearly one-dimensional ionic conductivity which is highest parallel to the  $c$  axis. Measurements we have made of the  $c$ -axis conductivity yield values of  $E \cong 0.83$  eV and  $\sigma_0 \cong 8 \times 10^4$   $(\Omega \text{ cm})^{-1}$ . Even in a polycrystalline arrangement of such crystals, the  $c$ -axis conductivity is expected to dominate and thus the temperature dependence should be activated with an energy of about 0.83 eV. The random orientation of the crystallite  $c$  axes with the electric field will reduce the conductivity at any temperature by a constant, geometric factor which produces a lower preexponential factor. If there were perfect ionic injection from one crystallite to another, this factor would be 0.5. However, if one considers the material of Raistrick *et al.*<sup>15</sup> to be a pure, polycrystalline mixture, then the injection process is apparently blocked frequently leading to a much lower  $\sigma_0$ . In any case, neither the ceramic actually produced by Raistrick *et al.*<sup>15</sup> nor the theoretical ceramic assembled from single crystals has values of  $E$  and  $\sigma_0$  appropriate for the 100% crystallinity values in this experiment. This is not too disconcerting, though, if the difference in preparation methods is considered. Our materials are formed by crystallization from the glass phase at elevated temperatures. Even small differences in density or thermal expansivity between the two phases can produce large stresses at their interface. Evidence for such stress in our materials is manifest by their proclivity to crack as they are cooled from the crystallization temperature. This stress leads to the possibility of an interface layer with properties different from either the glass or the bulk crystal. Further evidence for a layer of different properties comes from the report that titania is excluded from  $\beta$  eucryptite crystallized from the glass phase.<sup>14</sup> This is consistent with our observation of (roughly) 100-Å particles of titania located preferentially at the boundaries of the  $\beta$  eucryptite crystallites. Because of the evidence for a physically and chemically distinct interface layer, it is entirely possible that the crystallite conductivity is controlled by a low-conductivity surface layer. In this case, the crystallites would have an effective, isotropic bulk conductivity dependent upon the surface layer conductivity.

Another hypothesis of why our extrapolated 100% values are not those expected for pure ceramic  $\beta$  eucryptite has to do with impurities in the crystallites. If the Ti were effective in blocking all the  $c$ -axis channels in the crystallites, then the bulk crystalline conductivity would change so as to have a higher activation energy and possibly a higher preexponential factor. However, any Ti incorporated in the  $\beta$  eucryptite crystallites is expected to substitute for the Si or Al in their tetrahedral sites instead of occupying a site in the  $c$ -axis channels. Thus we consider this possibility to be less likely.

The above discussion of the unexpected values of  $E$  and  $\sigma_0$  for the highly crystalline materials and their probable cause has been largely independent of a specific conductivity model. We are now ready to consider a specific model and to discuss the consistency of the model assumptions with the measured material's properties.

#### B. Percolation model

We propose that the conductivity of the  $\text{LiAlSiO}_4$  glass-ceramic system may essentially be described by considering it to be a random binary mixture of crystallites in a glassy phase. In the temperature range of interest, the glass conductivity is always much higher than the effective, bulk conductivity of the crystallites. This, then, is a percolation problem in the sense that there are easy and hard paths by which the ions are conducted through the material. Because the spread of endpoint conductivities is less than a factor of  $10^6$ , the problem is one which may be reasonably solved in an effective medium approximation.<sup>16,17</sup> The effective medium theory appropriate for this problem has been worked out by Landauer.<sup>18</sup> Since considerable discussion of effective medium theory, particularly its derivation and limitations, already appears in the published literature<sup>16-21</sup> we shall give only a brief description of Landauer's continuum version here. He considers the conductivity in a continuous medium composed of two continuous, isotropic, different conductivity phases randomly interdispersed. The effective conductivity of the medium is determined self-consistently by assuming that each volume element is surrounded by an average environment instead of explicitly treating all possible environments. In notation suitable to our problem, Landauer's result may be written

$$\sigma(c, T) = \frac{1}{4} \sigma_c(T) [(2a - 1) - 3(a - 1)c + \{8a + [(2a - 1) - 3(a - 1)c]^2\}^{1/2}], \quad (1)$$

where  $c$  is the volume fraction of crystallites and  $a$  is the ratio of glass-to-crystallite conductivities

at any given temperature

$$a = a(T) = \sigma_g(T) / \sigma_c(T).$$

We take the conductivities of each pure phase to be thermally activated:

$$\sigma_g(T) = \sigma_{g0} e^{-E_g/kT}, \quad \sigma_c(T) = \sigma_{c0} e^{-E_c/kT}.$$

For the glass, we use values of  $E_g = 0.676$  eV and  $\sigma_{g0} = 183$  ( $\Omega \text{ cm}$ )<sup>-1</sup> as measured. Since we were not able to obtain a measurable sample of 100% crystallinity by our method, we have had to estimate values for this case. For values of  $E_c = 1.21$  eV and  $\sigma_{c0} = 1.5 \times 10^5$  ( $\Omega \text{ cm}$ )<sup>-1</sup> the effective-medium results for the preexponential factor and activation energy are shown in Fig. 5. As discussed by Pike *et al.*,<sup>22</sup> the effective medium conductivity will not have a simple activated form. However, it is approximately activated with preexponential factors and activation energies which vary slowly and smoothly with temperature. Our results were obtained by calculating the conductivity at fixed crys-

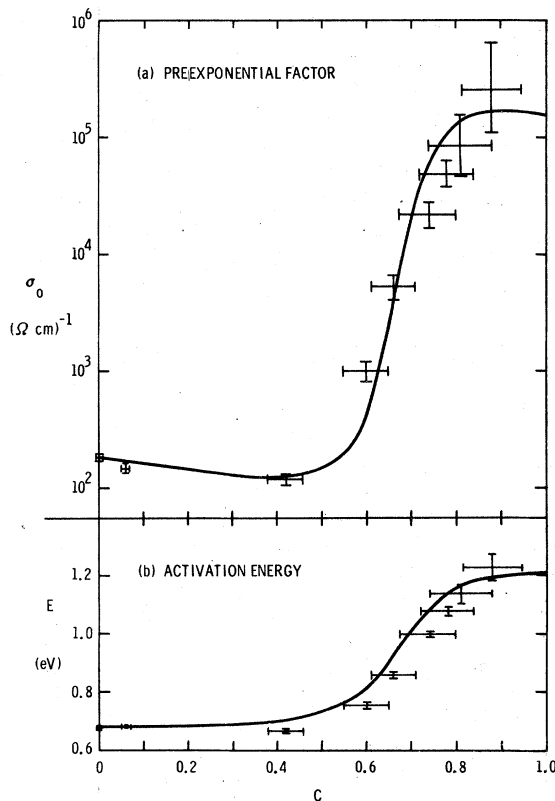


FIG. 5. Results of percolation model calculations. The solid lines show the calculated effective medium values of (a) the preexponential factor; and (b) the activation energy for the Li ion conductivity. The corresponding experimental values are also shown. Both parts of the graph have a common abscissa which is the volume fraction of crystallinity  $c$ .

tallinity fraction for values of  $10^3/T$  equal to 1.6 and  $2.0 \text{ K}^{-1}$  which are in the middle of the experimental range. Activation energies and preexponential factors were determined from these conductivities for many values of  $c$ . From Fig. 5 it can be seen that the overall fit to the data is quite good. Similarly, good agreement can be obtained only in a rather narrow range for crystallite parameters,  $E_c = (1.21 \pm 0.02) \text{ eV}$  and  $\sigma_{c0} = (1.5 \pm 0.4) \times 10^5 (\Omega \text{ cm})^{-1}$ . The principal disagreement between theory and experiment is seen to be the location of the critical crystallite fraction at which both  $E$  and  $\sigma_0$  begin to change rapidly. This is a well-known minor failure of effective medium theory that results from ignoring details of the strongly fluctuating environment near the critical concentration.<sup>19,20,23-25</sup> Nevertheless, the theory does yield a good, semiquantitative fit.

Physically, the data may be interpreted as follows. When small amounts of crystallite are added to (precipitated within) the glass, they act mainly to block ions from traversing their volume because of their much lower effective conductivity. Thus the ions which are measured during a conductivity experiment are moving through the glass phase. The temperature dependence, described by  $E$ , will remain that of the glass alone, but the geometric effect of the obstructing crystallites will decrease the conductivity slightly, and hence also  $\sigma_0$ . This situation prevails until the critical concentration is reached at which point the ions will no longer be able to utilize purely glass paths in crossing the material. In real systems, this critical concentration will obviously depend on details of particle shape and interparticle connections. These physical details are also ignored in Landauer's treatment which shows why the critical concentration is not predicted too well. As the crystallite concentration increases further, the temperature dependence of the crystallite regions begins to influence that of the total material,  $E$  tends to  $E_c$ , and the overall preexponential factor  $\sigma_0$  moves toward  $\sigma_{c0}$ .

We now want to address the questions of how well the assumptions of this model agree with the actual  $\text{LiAlSiO}_4$  glass-ceramic system and how the model could be applied to other glass-ceramics. One important assumption we made was that the conductivity of the glass phase remained constant independent of the crystalline fraction. This was because the chemical composition of the two phases is the same. However, in the high-crystallinity samples, this might be questioned due to the glass (at least partially) being enriched with the  $\text{TiO}_2$  which is excluded from the crystallites. The effect of this on the glass conductivity is unknown, but two separate considerations indicate that the

model fit will be only minimally affected. First, we know that the glass conductivity is not discernibly changed when the  $\text{TiO}_2$  concentration is changed from 0 to 2.8 mole%.<sup>1</sup> Second, it is in the high-crystallinity range that the glass conductivity affects the overall conductivity the least (within our model). Thus the  $\text{TiO}_2$  may change the glass conductivity somewhat, but the model should still be quite applicable.

Another assumption in our model is that the crystallite conductivity  $\sigma_c$  is constant independent of crystalline fraction. If  $\sigma_c$  is controlled by  $\text{TiO}_2$  impurities within the crystallites, and if the  $\text{TiO}_2$  concentration is saturated (as indicated), then this should be a good assumption. However, if the bulk conductivity is only "effective," controlled by a surface layer, then  $\sigma_c$  ought to vary directly as the crystallite size.<sup>26</sup> The average crystallite size does change in samples from  $\sim 0.3 \mu\text{m}$  at 13% crystallinity to  $\sim 1.2 \mu\text{m}$  at 81%. By assuming a linear variation of crystallite size, and hence conductivity, with crystalline fraction, we have recalculated the effective medium conductivity by using the same conductivity values as before for  $c = 0$  and 1.0. We find very little difference from the curves in Fig. 5 except that the calculated preexponential factor undershoots somewhat the data point at  $c = 0.42$ . Thus for the conditions of our experiment, this complication has a negligible effect on the model fit. While on the subject of crystallite size, we note that the  $\text{TiO}_2$  at the crystallite surface probably helps to limit the grain size in two ways. For an isolated crystallite to expand, it must exclude ever increasing concentrations of  $\text{TiO}_2$  from the surrounding glass layer which requires even longer times for the  $\text{TiO}_2$  to diffuse away. For two nearby crystallites growing toward each other, the presence of the  $\text{TiO}_2$  enriched layer will tend to prevent them from joining into a larger particle without a low conductivity intraparticle barrier. That is, the crystallization process is schematically like a random collection of expanding balloons which preserve their membrane interface even as their contact area increases. Thus polycrystalline clusters in our particular material are treated as a joined collection of small grains rather than one large grain with a proportionately larger effective conductivity.

As we have already noted, the glass-ceramic system we have chosen to study is rather special in that the chemical composition of the two phases is nearly the same and the structure of each phase remains constant for all crystalline fractions. In other systems, such as have been studied in the past, this is not the case. To apply our model to other glass-ceramics would require that the com-

position and conductivity of each phase be known for each crystallinity fraction.

As a final comment, we reverse the emphasis and note that the  $\text{LiAlSiO}_4$  glass-ceramic system is probably the most ideal actual realization of Landauer's mathematical model to appear in the literature. This is because the material can properly be treated as a two-phase continuum (instead of a lattice) and the conductivity difference between these phases is large enough to produce significant differences with changing volume fractions.<sup>27</sup>

## VI. SUMMARY AND CONCLUSIONS

We have made a series of glass-ceramics, all with the same composition ( $\text{LiAlSiO}_4$ ) for the glass and crystalline phases, but differing from each other by the fraction of crystalline phase present. X-ray techniques are used to quantitatively measure the crystallinity and to determine that the crystallites are  $\beta$  eucryptite in all samples. Transmission electron micrographs yield information about the grain size and about accumulation of the  $\text{TiO}_2$  nucleating agent at the crystallite boundaries. Measurements of the lithium ion conductivity versus temperature reveal an Arrhenius form for all the glass ceramics.

There are two aspects of the conductivity results which are particularly interesting. First, the conductivity of the highly crystalline glass-ceramics does not approach the expected values either derived from single-crystal results or obtained on pure ceramic (polycrystalline) materials. In the glass-ceramics, the precipitation of crystallites from within the glass probably causes a highly strained glass-crystallite interface. We have argued that in our glass-ceramics, the strain and/or the  $\text{TiO}_2$  enrichment could produce a low-conduc-

tivity layer. This would cause the conductivity of the crystalline regions to be other than expected. The second interesting feature is that the conductivity changes in a nonsimple manner with increasing crystallinity. The most notable aspect of this variation is the abrupt change of both the activation energy and preexponential factor near 55% crystallinity. To account for the dependence of conductivity on crystallinity, we have used a percolation model which is solved within the effective medium approximation. Physically, the results indicate that within the glass-ceramic, the ions move almost exclusively through the glass phase until a critical crystalline concentration is reached. Beyond this point, the ions must also traverse the lower-conductivity regions in crossing the materials. By the use of such modeling, excellent agreement is obtained with our experimental data.

This is the first application of percolation theory to the description of ionic conductivity in glass-ceramics. Although the  $\text{LiAlSiO}_4$  materials examined here were nearly ideal for such studies, it should be possible to apply this type of modeling to other glass-ceramic systems.

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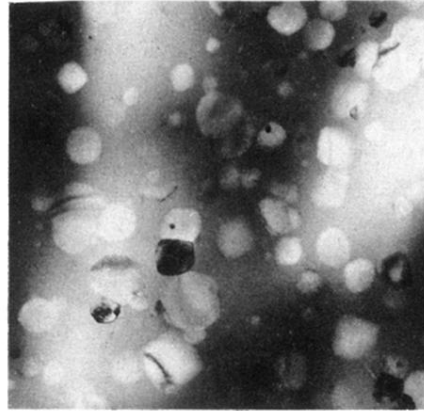
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- <sup>27</sup>This approach has previously been applied to self-diffusion in silicon-germanium substitutional alloys (Ref. 22). In this case, the discrete lattice aspects of the problem cannot be neglected. Nevertheless, there is surprisingly good agreement between effective medium theory and exact numerical predictions for the diffusivity.



(a)

1  $\mu\text{m}$



(b)

1  $\mu\text{m}$

FIG. 1. Transmission electron micrographs of  $\text{LiAlSiO}_4$  glass-ceramics with 2.8-mole%  $\text{TiO}_2$  as a nucleating agent. (a) Micrograph of the 13% crystalline material with  $\sim 0.3\text{-}\mu\text{m}$  crystallites of  $\beta$  eucryptite; (b) micrograph of the 81% crystalline material with  $1.2\text{-}\mu\text{m}$  crystallites of  $\beta$  eucryptite. The small dark areas located primarily in the grain boundaries of the  $\beta$  eucryptite crystallites [in part (b)] are  $\sim 50\text{-}100\text{-}\text{\AA}$   $\text{TiO}_2$  crystallites.