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Effect of devitrification on the ionic diffusion of Li-disilicate

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Abstract

A simple theoretical model has been developed for describing the variation of diffusion of ions in an initially homogeneous glass as it transforms into a two-phase structure. The model is applicable to those microstructures in which the second phase grows as a discontinuous dispersion without affecting the diffusion properties of the glassy matrix. The validity of the model is demonstrated by the measurement of ionic conductivity and of diffusion-induced ^{7}Li nuclear spin relaxation during the devitrification of Li-disilicate, containing 0 and 1 mol% P_2O_5, respectively. Evaluation of the data yields the basic parameters of devitrification.

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1. Introduction

Diffusion of mobile (typically network modifiers) ions is a fundamental process in common glasses, which determines their several important properties such as electrical conductivity, dielectric loss, chemical durability, ion exchange for strengthening or graded optical profile, gas containment or permeation [1]. For modeling these properties, generally the glass is assumed to be a homogeneous single phase solid through which the ions diffuse by a thermally activated mechanism [2]. In general, this assumption will be incorrect when the glass consists of two or more phases. There are two important examples where, in fact, a multi-phase structure is expected as the ions have to move through the microstructure in a complicated manner: (a) in a partly crystallized glass, and (b) in a phase separated glass. Indeed, experiments confirm that ion diffusion can differ in a devitrified glass as compared to that in a homogeneous glass [3,4]. So far no information is available on exactly how the ion transport depends on the extent of transformation of glass into a two-phase structure by any mechanism. Therefore, in this paper we analyse the effect of the time and temperature dependence of gradual devitrification on ion transport by combining semi-empirical models of percolation and crystallization. The present analysis may be applicable also to other similar situations such as to diffusion in a glass that is undergoing phase separation.

2. Theoretical model

Let us consider ionic conductivity as a convenient measure of ion diffusion in a homogeneous glass that is being gradually devitrified to a fully crystalline glass-ceramic. The glass is assumed to crystallize congruently by nucleation and growth,

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so that there is no change in chemical composition of the sample with time. Thus the crystalline phase grows as randomly dispersed islands in the glassy matrix. Initially the crystalline regions are disconnected, but with increasing volume fraction of the crystalline phase, they would begin connecting with one another. Ultimately the glass phase is consumed completely and its volume fraction, p, is reduced to zero.

As is typically the case, we assume the conductivity of glassy phase, σ_g, to be much larger than that of the crystalline phase, σ_c, so that the ions move preferentially through the glassy phase. Devitrification of Li-disilicate is a classic model example that satisfies these conditions [5] (see Fig. 2). The contribution of grain or phase boundaries to the total conductivity is assumed to be negligible. As a result, although neither σ_g nor σ_c changes with time, the measured dc conductivity of the sample, σ_{dc}, evolves from σ_g to σ_c as the glass transforms to glass-ceramic. At a given instant of devitrification, t, the flow of ions can be treated as a percolation through the corresponding two-phase microstructure, which primarily depends on the fraction of glass (p) remaining in the sample at that time. The percolation conductivity of such a two-phase microstructure has been calculated by Monte Carlo computer simulations [6]. Whereas the exact expression for conductivity may depend on the details of constraints imposed on the percolation process, it has a general form that can be separately written for two regions by the use of the effective medium approach [7]:

Region (*a*): The conductivity is dominated by the glassy matrix. In this case the glass phase is continuous from one electrode to the other (i.e. $p > p_c$), and

$$\sigma_{dc} = \sigma_0(T)(p - p_c)^\gamma, \tag{1}$$

with

$$\sigma_g = \sigma_0(1 - p_c)^\gamma. \tag{2}$$

Here p_c is a constant called percolation threshold above which the continuity of the glass phase is maintained. p_c is $\sim$0.1 to 0.3, and that of γ is $\sim$1.3 to 1.7 depending on the specifics of percolation [7]. As $(1 - p_c)^\gamma =$ constant, σ_g (T) is proportional to $\sigma_0(T)$.

Region (*b*): The conductivity is dominated by the crystalline phase that maintains continuity through the sample i.e., $p < p_c$. Then,

$$\sigma_{dc} = \sigma_c(T)/(1 - p/p_c)^\alpha, \tag{3}$$

where $\alpha \cong 1$ for percolation that is equally probable in the three-dimensions [7].

In a devitrification experiment the microstructure of glass changes continuously as the crystalline phase continues to grow from the glassy matrix. That is, the parameter p in Eq. (1) or (3) is time dependent. The kinetics of this isothermal transformation at a given temperature are given by the well-known Johnson–Mehl–Avrami relation [8,9]

$$p = \exp[-\{K(T)t\}^m], \tag{4}$$

where the rate constant

$$K(T) = K_0 \exp[-E_d/kT]. \tag{5}$$

Here K_0 is a pre-exponential factor and E_d is the activation energy for the fundamental devitrification process. The constant m is 1, 2 or 3 depending on whether the crystals grow in one-, two-, or three-dimensions, respectively. If nucleation of the crystalline phase occurs together with its growth, the corresponding m should be increased by 1. $m = 3$ has been observed for devitrification in the interior of the Li_2O–SiO_2 system [10]. To determine the time dependence of σ_{dc} while the sample is undergoing isothermal devitrification, we insert Eqs. (4) and (5) into Eqs. (1) and (3). The result gives σ_{dc} as a function of time (t) and temperature (T) for the two regions that are now separated by $t = t_c$ corresponding to $p = p_c$. Thus we get the desired results as

$$\textit{Region (a)} \quad (t < t_c): \ \sigma_{dc}(T,t) = \sigma_0(T) \{\exp[-(K(T)t)^m] - p_c\}^\gamma, \tag{6}$$

$$\textit{Region (b)} \quad (t \geqslant t_c): \ \sigma_{dc}(T,t) = \sigma_c(T)/ \left\{1 - p_c^{-1}\exp[-(K(T)t)^m\right\}^\alpha. \tag{7}$$

Here the percolation time t_c is related to the percolation threshold p_c by σ_{dc}(region (a)) = 0

$$t_c(T) = [-\ln p_c]^{1/m}/K(T). \tag{8}$$

Fig. 1 shows schematically the variation of σ_{dc} with the normalized time t/t_c for the two regions (a,b). Here we have taken $m = 1$ and 3, respectively, $p_c = 0.2$, $\gamma = 1.5$, $\alpha = 1$, $\sigma_0 = 1$ (a.u.), and $\sigma_c = 10^{-3}\sigma_0$ [7]. As expected, there is a discontinuity in σ_{dc} at $t = t_c$. In practice, however, σ_{dc} is measured continuously across the two regions, as indicated by the solid curves in Fig. 1. Finally, we expect from Eq. (8) that t_c depends on temperature. If we observe σ_{dc} during isothermal devitrification transformation at different temperatures, and determine corresponding times $t_c(T)$ according to Fig. 1, the following relation should be valid (see Eqs. (5) and (8)):

$$\ln t_c(T) = (E_d/k)1/T + \ln c, \tag{9}$$

where

$$c = (1/K_0)(-\ln p_c)^{1/m}. \tag{9a}$$

Eq. (9) provides the basis of a simple method for experimentally determining the basic parameters of devitrification. For example, the devitrification rate constant and its activation energy can be obtained from the intercept and slope of a plot of ln t_c vs $1/T$ which can be fit by the Arrhenius relation (9). Rather than observing growth kinetics by measurements of microstructure, we obtain similar information by much more convenient isothermal measurement of conductivity or some other property such as diffusion-induced nuclear spin relaxation [11] that is directly related to the ionic diffusion.

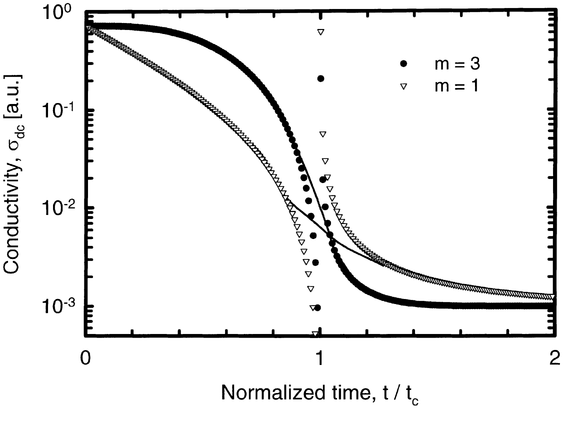

Fig. 1. Time dependence of the conductivity σ_{dc} during one-dimensional ($m = 1$) and isotropic ($m = 3$) devitrification as given by Eqs. (6) and (7). Solid lines: smoothened singularity at t_c (see text).

3. Experimental details

The experiments were performed on nominally Li-disilicate glasses of composition 33.3 $Li_2O \cdot$ 66.7 SiO_2 (LiSi) and 36 $Li_2O \cdot 63\, SiO_2 \cdot 1\, P_2O_5$ (LiSiP). The glasses were prepared by the melt-quench method, starting with a batch of reagent grade Li_2CO_3, SiO_2, and Li_3PO_4 powders in appropriate ratio. After the powders had reacted at 1150°C, the melt was homogenized at 1450°C for 2 h. Bubble free glass was obtained by casting the melt in a copper mold. The cast pieces were annealed at 300°C for 6 h to relieve thermal stresses, and then slowly cooled to room temperature. Since P_2O_5 serves as a nucleating agent assuring uniform nucleation throughout the sample the devitrification experiments on LiSiP were carried out using one-stage annealing treatment. Unlike LiSiP, the devitrification experiments on LiSi were performed by a two-stage annealing procedure. To create a sufficient number of homogeneously distributed nuclei the samples were annealed at 475°C for 5 h. Then, the effect of devitrification on conductivity and nuclear spin relaxation was measured at different temperatures. The distribution of the crystalline phase was observed by optical microscopy of the sample that was quenched to room temperature at various stages of devitrification. The dc conductivity, σ_{dc}, was measured with an impedance meter (Schlumberger SI-1260) and a sensitivity improving electrometer-type preamplifier (Chelsea Dielectric) operating between 10 μHz and 10 MHz. The ^7Li nuclear spin relaxation (NSR) rates, $1/T_1$, were determined at 78.7 MHz from the time evolution of the nuclear magnetization with an upgraded coherent pulse NMR spectrometer (Bruker SXP 4-100) using the saturation-recovery technique [12]. In contrast to glassy and completely crystallized samples, the magnetization was found to decay non-exponentially in partially devitrified samples. Then, a mean NSR rate was obtained from the data. Details of the NMR experiments are presented elsewhere [13]. One should note that unlike conductivity the NSR method does not use electrodes, thus avoiding electrode polarization problems.

4. Results and discussion

The dc conductivity of the starting glasses and fully devitrified glass-ceramics is depicted in Fig. 2(a) as a function of temperature. The Arrhenius relation $\sigma_{dc}T \propto \exp(-E/kT)$ with $E_g = 68$ kJ/mol and $E_c = 133$ kJ/mol for LiSi, and $E_g = 65$ kJ/mol and $E_c = 94$ kJ/mol for LiSiP is fitted to the data with a correlation coefficient $R = 0.99$, and the data confirm that in the entire temperature region, $\sigma_g \gg \sigma_c$. Moreover, the data demonstrate the effect of a small amount of phosphorous on the ionic diffusion in glassy as well as in crystalline Li-disilicate. The microstructure of gradually devitrified glass samples observed by X-ray diffraction [14] and optical micrographs [15] shows that the crystalline phase grows randomly but uniformly throughout as nearly spherical particles. Thus the theoretical model developed above should be applicable to our samples. Fig. 3 shows the isothermal variation of the dc conductivity observed in LiSi as a function of devitrification time at different temperatures. The shape of the curves agrees approximately with the theoretical predictions shown in Fig. 1, thus providing a qualitative confirmation for the model. In particular, the percolation times, t_c, can be determined from the curves. In contrast to the prediction of the model, however, a monotonic decrease of σ_{dc} was measured for $t < t_c$. This decrease is probably caused by a variation of the diffusion properties of the glassy matrix during devitrification, which is not taken into account by the model. Moreover, unlike the curves shown in Fig. 3, the σ_{dc} plots should cross each other for $t \gg t_c$ according to the temperature dependence of σ_c shown in Fig. 2(a). However, the final crystalline state depends on the annealing temperatures. As predicted by Eq. (9) the representation of t_c can be fit with an Arrhenius relation with correlation coefficients $R = 0.98$ (see Fig. 5); the slopes give $E_d = 299 \pm 20$ kJ/mol for LiSi and $E_d = 225 \pm 20$ kJ/mol for LiSiP, respectively. The former agrees with the 272 ± 42 kJ/mol obtained from positron annihilation [10], 299 ± 15 kJ/mol by differential thermal analysis [16], or 282 kJ/mol by reflection optical microscopy [17]. The difference between the observed values for E_d suggests that even a small amount of phosphorous assists considerably the

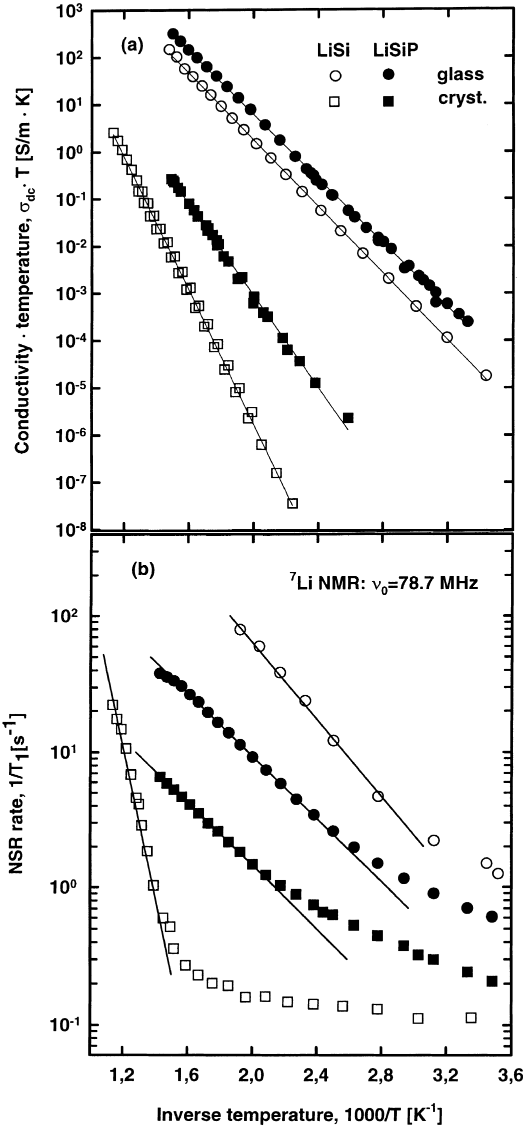

Fig. 2. Plots of: (a) dc conductivity ($\sigma_{dc}T$); (b) ^{7}Li NSR rate (T_1^{-1}), in glassy and fully crystallized two nominally Li-disilicate containing 0 (LiSi) and 1 mol% P_2O_5 (LiSiP). Arrhenius relations are fitted to the data with a correlation coefficient $R = 0.99$ (a) and $R = 0.98$ (b), respectively.

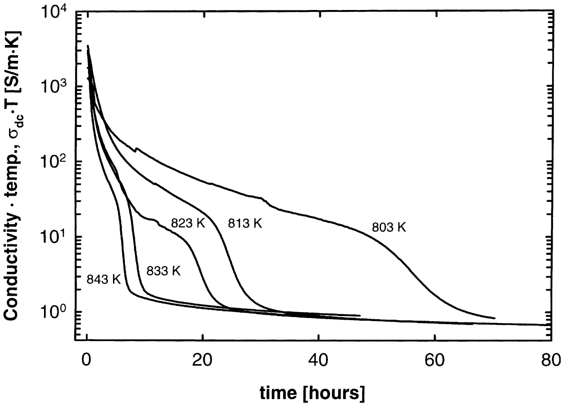

Fig. 3. Isothermal time evolution of dc conductivity (σ_{dc}) of LiSi during devitrification at different temperatures.

devitrification process. Furthermore, by means of Eq. (9a) we estimate from the data $K_0(\mathrm{LiSi}) = 2\times10^{14}\ \mathrm{s}^{-1}$ and $K_0(\mathrm{LiSiP}) = 1\times10^{10}\ \mathrm{s}^{-1}$ for the pre-exponential factor (Eq. (5)) using $m = 3$ and $p_c = 0.2$ as reasonable parameters [5,10].

From our previous studies of Li-ion transport in glasses, it is well established that the observed ^{7}Li NSR rate, T_1^{-1}, at temperatures >300 K arises from the diffusive motion of Li$^+$ while at temperatures <300 K the relaxation is due to localized low-frequency fluctuations [11,13,18]. The fluctuation-dissipation theorem implies that the ionic ac conductivity σ_{ac} is proportional to T_1^{-1}/T if the ionic jump rate is less than the frequency used in either measurement. Hence, as depicted in Fig. 2(b), the ^{7}Li NSR rates observed in LiSi and LiSiP are fit by the Arrhenius relation above room temperature analogous to σ_{dc}. However, because of the frequency dependent conductivity dispersion commonly observed in glassy as well as in disordered crystallized materials [19] the slope of the curves results in smaller activation energies, V, compared to the energies, E, obtained from σ_{dc} in Fig. 2(a): We found $V_g = 27$ and $V_c = 107$ kJ/mol for LiSi, and $\mathrm{V_g} = V_c = 22.2$ kJ/mol for LiSiP. According to the coupling model the two energies are linked by the exponent $\beta \leqslant 1$ of the stretched-exponential function describing the diffusion process $V = \beta E$ [20]. If the frequency dispersion does not change with the degree of devitrification, σ_{dc}/σ_{ac}, and, therefore, $\sigma_{dc}/\mathrm{T}_1^{-1}$ are expected to remain constant during any isothermal devitrification treatment . In other words, the time dependence of $1/T_1$ should follow that of σ_{dc}, which is indeed shown by the NSR measurements on LiSiP (Fig. 4). In fact, as depicted in Fig. 5, the percolation times, t_c, obtained from ^{7}Li NSR measurements (see Fig. 4) are in accord to within ±20% with those determined from ionic conductivity. An

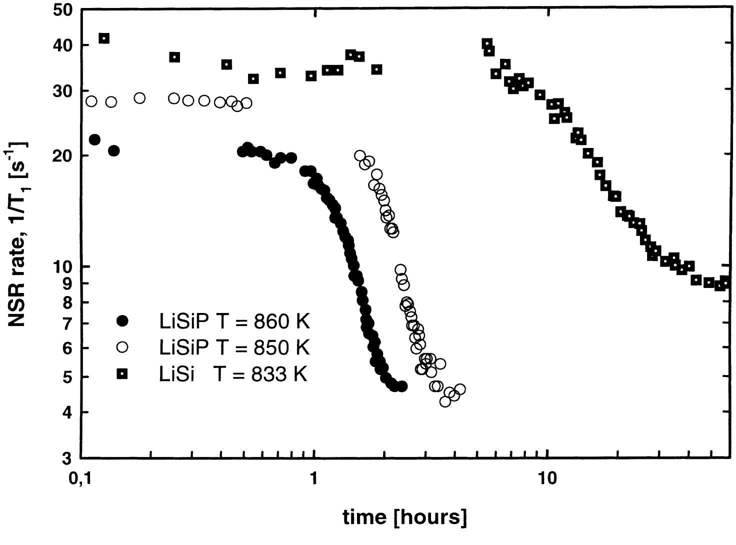

Fig. 4. Isothermal time evolution of ^{7}Li NSR rate in LiSiP and LiSi during devitrification.

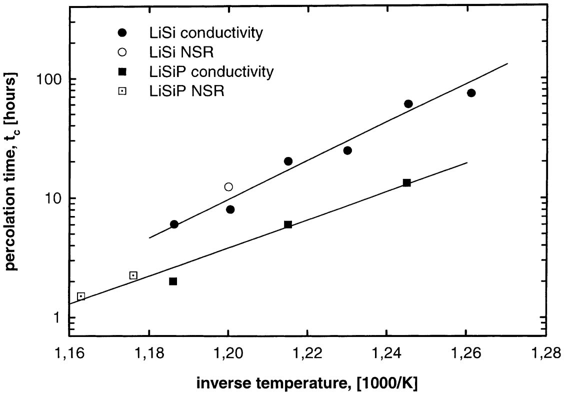

Fig. 5. Percolation times t_c as obtained from the isothermal time dependence of conductivity and ^{7}Li NSR (see Figs. 3 and 4). The Arrhenius relation (9) is fitted to the data with a correlation coefficient $R = 0.98$.

extended study is in progress in order to determine further details of the observed differences between the devitrification parameters obtained for LiSi and LiSiP .

5. Summary

We have developed a theoretical model for describing diffusion in glass that is being transformed from a single homogeneous phase to a two-phase structure. In its present form the model is limited to the situations where the second phase develops as a discontinuous dispersion without affecting the diffusion in the glassy matrix. Moreover, the approach is insensitive to the microscopic mechanism of phase transformation. The measurements of ionic conductivity and ^{7}Li NSR confirm the validity of the model for ion diffusion in Li-disilicate glasses during devitrification.

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