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Single particle jumps and correlated ionic motions in glass-ceramics *

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Using impedance spectroscopy, the ion transport in poorly Li-conducting aluminosilicate glass ceramics and their precursor glasses has been measured for temperatures 50 K $< T <$ 550 K and covering a frequency range of more than 14 decades from 10 mHz up to 3 THz. In addition to the familiar cooperative ionic motion dominating at high temperatures, for the first time dielectric relaxation due to elementary hopping processes is observed well below room temperature.

The search for materials with maximum electrical conductivity at room temperature, suitable for applications as solid state electrolytes, has stimulated a number of theoretical and experimental studies of ionic transport in amorphous and crystalline solids [1]. Despite these efforts, our current state of understanding of ionic conductivity in these materials is incomplete and generally accepted theoretical concepts are still missing [2]. Hence such basic issues as to the importance of steric hindrance versus Coulombic repulsions, the question of a common physical origin of ac and dc conductivities, and sometimes even the relevance of hopping processes are still matters of controversy [3–5].

The various theoretical approaches to ionic transport, although quite different in their assumptions and computational (approximative) procedures, often yield surprisingly similar predictions concerning the frequency- and temperature-dependent electrical conductivity. This circumstance hampers the identification of the relevant theoretical model and hence the identification of the appropriate microscopic conduction mechanism. Consequently it is highly desirable to devise experiments which are able to track down local hopping processes in order to determine the interplay of elementary, local ion jumps and transport properties due to the interacting charge carriers.

In the following we present what we believe may be the first experimental observation of the elementary hopping process using the technique of broadband impedance spectroscopy. The ionic conductors used for this study are amorphous as well as partly (70%) recrystallized aluminosilicate glasses of identical overall composition which contain 7.8 mol% Li_2O with Li as the mobile species. The composition of the Li_2O–Al_2O_3–SiO_2-based commercially available glass ceramic (Zerodur) has been reported previously [6].

Applying various experimental techniques, the complex conductivity $\sigma = \sigma' + i\sigma''$ or dielectric constant $\epsilon = \sigma/(i\omega\epsilon_0)$ (with ϵ_0 being the permit-

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* In memoriam F. Hufnagel.

tivity of free space) was measured for temperatures 50 K $\leq T \leq$ 550 K and over a wide frequency range covering more than 14 decades (10 mHz $\leq f \leq$ 3 THz). For the impedance analysis and reflectometric measurements below 1 GHz, gold electrodes were deposited onto both faces of disc-shaped samples. Space charge effects associated with these electrodes which were observed to show up in our low conductivity specimen at elevated temperatures and at very low frequencies did not affect the results presented in this paper. For the measurements at higher frequencies, microwave radiation was generated using semiconductor diodes and molecular lasers and was transmitted through wedge-shaped specimens using a procedure that avoids perturbations due to multiple reflections. The conductivity was calculated from the transmitted microwave power as monitored with Golay detectors [7]. A full account of the experimental procedures will be published elsewhere [8].

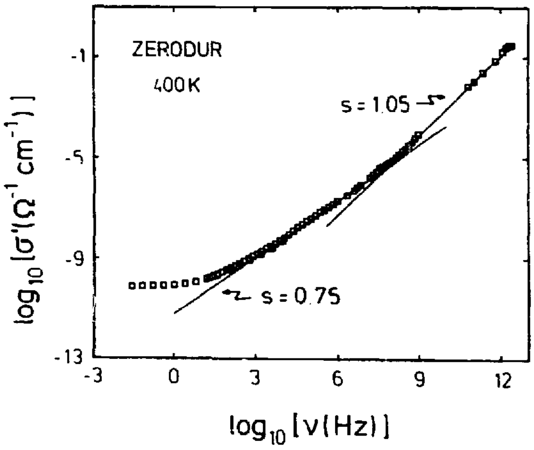

Fig. 1. Double logarithmic plot of conductivity vs. frequency. σ' was measured for Zerodur glass-ceramic at a temperature of $T = 400$ K. The solid lines represent power laws with slopes s as indicated.

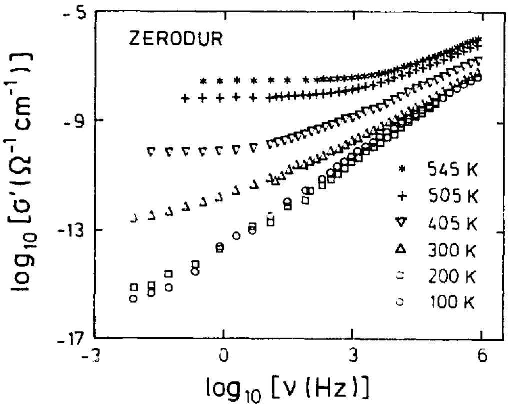

Fig. 2. Conductivity logσ' of the Li-conducting aluminosilicate glass-ceramic versus the logarithm of frequency as measured for several temperatures.

The real part of the electrical conductivity of the glass ceramic as measured at $T = 400$ K is presented in fig. 1. It is seen that σ' exhibits the typical ω^s-dependences. At high frequencies, we find $s = 1.05 \pm 0.05$, i.e., $\epsilon'' \approx$ const.; the constant loss region [2] shows up in a range of about 4 decades. At medium frequencies (10 kHz $\leq f \leq$ 100 MHz), a constant slope of $s = 0.75 \pm 0.02$ is found. Finally the frequency exponent $s = \mathrm{d}\log\sigma'/\mathrm{d}\log\omega$ gradually decreases until the dc plateau is reached, i.e., $\sigma = \sigma_{\mathrm{dc}}$. Figure 1 clearly demonstrates the existence of a well defined ω^s-region (with $s < 1$). A power law behaviour at intermediate frequencies was recently shown by Maas et al. to arise in models for ionic conductivity in which only the effects of disorder and Coulomb interaction are taken into account [9]. The existence of a true power law regime which is the signature of correlated ionic transport is however much less obvious if only data in a limited range of frequencies are considered (see, for example, the data in ref. [10]). The fact that in a restricted spectral range no well defined power laws are obvious is demonstrated in fig. 2 where conductivity data measured only in the lower 8 frequency decades are plotted for a number of temperatures. For $T \geq 250$ K, the dc conductivity is readily obtained from the low frequency plateau and is shown in an Arrhenius plot (fig. 3). Using this plot, the activation energy, E_{dc}, governing the dynamics of the correlated ionic motions has been determined according to

$$\sigma_{\mathrm{dc}} = \sigma_0 \exp(-E_{\mathrm{dc}}/k_{\mathrm{B}}T). \tag{1}$$

We find $E_{\mathrm{dc}} = 0.75 \pm 0.02$ eV which is typical for aluminosilicate systems [11,12]. From an Arrhenius plot of the frequencies corresponding to the maxima of the imaginary part of the electrical modulus, defined by $M = 1/\epsilon$, we find an activation energy of $E_M = 0.77 \pm 0.03$ eV [13], in good agreement with that determined from dc conductivity.

For temperatures below ambient, the dc plateau is no longer clearly defined and the electrical conductivity as measured in the audio and sub-audio frequency ranges is extremely small (see fig. 2). More detailed insights into the low temperature properties can be gained from fig. 4 which shows the dielectric loss, $\epsilon''(T)$, of the glass-ceramic (a) as well as its precursor glass (b) for several measuring frequencies. Frequency-dependent dielectric loss peaks, the signature of dipolar relaxation processes, show up in the glass-ceramic, but they are less well developed in the fully amorphous material.

In the following, we provide evidence that this dielectric relaxation is due to single particle hops of Li ions in local double well potentials. Double well potentials are a well known structural feature of several crystalline compounds in the Li_2O–Al_2O_3–SiO_2 system. For example, in β-eucryptite ($LiAlSiO_4$) or β-spodumene ($LiAlSi_2O_6$) there are respectively three and four paired Li sites (with an average site occupancy of 50%) in the unit cell which are only about 1.5 Å apart [14,15]. The (local) energy barrier, E_l, separating the two sites in the pair is expected to be much better defined in these crystals as compared with the partly or fully amorphous compounds. Here an increasing distribution of local structural environments may lead to a broadening of the relaxation peaks, as is indeed the case (see fig. 4). For the precursor glass, the peaks are already largely obscured by the dc conduction process. Therefore only for the glass-ceramic can the energy barrier against the local hopping be evaluated. As shown in fig. 3, we find $E_l = 0.18 \pm 0.01$ eV.

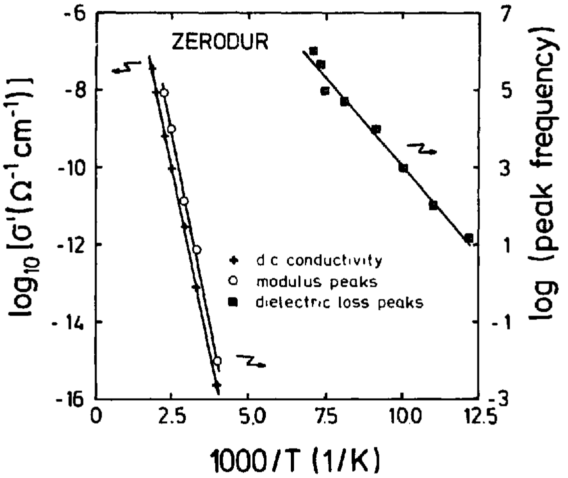

Fig. 3. Logarithm of the dc conductivity (+, left-hand scale) and of characteristic frequencies (right-hand scale) plotted versus inverse temperature. The characteristic frequencies were determined from the modulus peaks (○, yielding E_M) at high temperatures and from the dielectric loss peaks (■, yielding E_l) at low T (cf. fig. 4 (a)). The solid lines are calculated using the energy barriers $E_{dc} = 0.75$ eV, $E_M = 0.77$ eV and $E_l = 0.18$ eV.

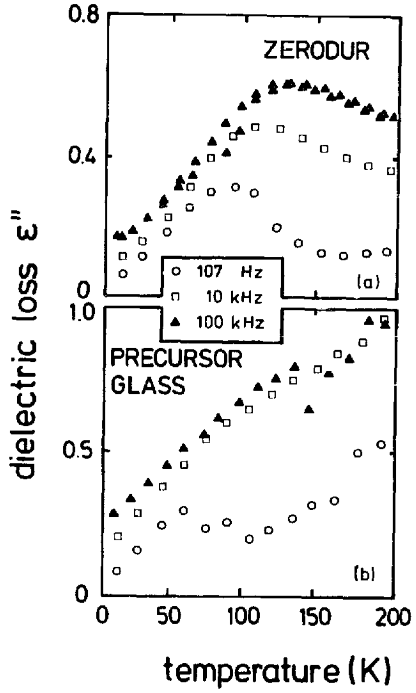

Fig. 4. Dielectric loss, $\epsilon''(T)$, for the glass ceramic (a) and its precursor glass (b) as measured for various audio frequencies.

It may now be asked whether the local process seen at low temperatures is related to the cooperative ionic transport which governs the electrical response at high T. It seems plausible that the collective motion of the Li ions requires the correlated excitation of the charge carriers over the local barriers. Under the assumption that the relaxation rate is constant for the single ion jumps, but slows down according to $t^{-(1-\beta)}$ as soon as cooperativity sets in, it is easy to show that [16]

$$E_{\mathrm{l}} = \beta E_{\mathrm{dc}}. \tag{2}$$

The relation of the cooperativity parameter $1-\beta$ (which describes the dynamics in the time domain) to the frequency exponent is $s = 1-\beta$. Using $s = 0.75$ (see fig. 1), i.e., $\beta = 0.25$, we find excellent agreement with $E_{\mathrm{l}}/E_{\mathrm{dc}} = 0.24$ as predicted by eq. (2). These considerations provide additional support for the assignment of E_{l} as the elementary barrier.

It should be emphasized that the aluminosilicate glass-ceramics investigated in the course of this work are one of the few ionic conductors (besides, for example, Na-β-alumina [17] and β-AgI [18]) for which a cooperativity crossover has been observed experimentally. The concept of cooperativity crossover is by no means new and has long been advocated in the coupling scheme of Ngai [16], but similar concepts [19] have recently been found to be inherent in independently developed theoretical frameworks, such as the cluster relaxation model of Chamberlin [20] or the disordered Coulomb lattice gas model by Maas et al. [9].

At first glance it may therefore appear surprising that previously the phenomenon has not been observed more frequently. There are, however, a number of reasons which make plausible why the elementary process usually escapes detection. First, as has been demonstrated above (fig. 4), the relaxation effects are much more pronounced in glass ceramics than in glasses [21], the latter having received much more attention in the literature. Also, even in glass-ceramics, the relaxation peaks may be obscured by the presence of collective ionic transport, i.e., in good ionic conductors.

To summarize, our broadband impedance spectroscopic investigation of lithium aluminosilicate glass ceramics has revealed the existence of a power law regime ($\sigma' \sim \omega^s$), located between the dc plateau at low frequencies and the constant loss region ($\sigma' \sim \omega$) at high frequencies. At low temperatures, the collective motion of the mobile charge carriers is drastically reduced and we observe dielectric loss peaks due to single ion hops in localized double well potentials. The collective and elementary relaxation processes are both thermally activated. In the framework of the phenomenological coupling model, the cooperative barrier, E_{dc}, and the frequency exponent, s, have been used to predict the local activation energy, E_{l}. Excellent agreement with the experimentally determined potential barrier is achieved.

Further studies should focus on ceramics with different degrees of crystallinity and on ceramics which are based on other network formers.

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