

## Fast Interfacial Ionic Conduction in Nanostructured Glass Ceramics

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The hopping movements of mobile ions in a nanostructured  $\text{LiAlSiO}_4$  glass ceramic are characterized by time-domain electrostatic force spectroscopy (TDEFS). While the macroscopic conductivity spectra are governed by a single activation energy, the nanoscopic TDEFS measurements reveal three different dynamic processes with distinct activation energies. Apart from the ion transport processes in the glassy and crystalline phases, we identify a third process with a very low activation energy, which is assigned to ionic movements at the interfaces between the crystallites and glassy phase. Such interfacial processes are believed to play a key role for obtaining high ionic conductivities in nanostructured solid electrolytes.

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The design of highly conductive solid electrolyte materials is an important prerequisite for many applications in the field of solid state ionics, such as microlithium batteries and large-area electrochromic windows. Today, many research groups work on the preparation of heterogeneous solid electrolytes with complex structures on nanoscopic or mesoscopic length scales. The internal interfaces in these materials have, in general, a strong influence on the ionic conductivity. For instance, nanocrystalline electrolytes exhibit often a considerably higher ionic conductivity than their microcrystalline counterparts [1]. In addition, the conductivity can be improved by adding nanocrystalline insulators. Indris and Heitjans found that the ionic conductivity of  $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$  nanocomposites reaches a maximum if the amount of conducting  $\text{Li}_2\text{O}$  and insulating  $\text{B}_2\text{O}_3$  nanoparticles is similar [2]. This suggests that fast lithium ion conduction takes place at the interfaces between the dissimilar nanoparticles. The same behavior was observed in copper-ion conducting  $\text{CuBr}-\text{TiO}_2$  and  $\text{CuBr}-\text{Al}_2\text{O}_3$  composites [3,4]. Sata *et al.* prepared hetero-layered films composed of the fluoride ion conductors  $\text{BaF}_2$  and  $\text{CaF}_2$  and found that the ionic conductivity of the films increases strongly with the density of interfaces [5,6]. In the case of salt-in-polymer electrolytes, Scrosati *et al.* observed that the dispersion of  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ , or  $\text{SiO}_2$  nanoparticles leads to a large increase of the ionic conductivity [7,8].

In the case of glassy electrolytes partial crystallization can lead to a conductivity enhancement. Examples are silver ion conducting  $0.57\text{AgI} \cdot 0.29\text{Ag}_2\text{O} \cdot 0.14\text{V}_2\text{O}_5$  glass ceramics [9] and lithium ion conducting  $\text{LiAlSiO}_4$  glass ceramics [10]. Since in both systems the ionic conductivity of the crystallites is lower than that of the glassy phase, the conductivity enhancement can only be explained

by postulating a third phase with a high ionic conductivity, namely, the interfacial area between the crystallites and the glassy phase. When the size of the crystallites is small, a large amount of interfacial area exists, and fast ionic conduction in these areas may have a significant influence on the overall conductivity.

Despite the large amount of heterogeneous solid electrolytes that have been investigated, the mechanisms of ionic conduction, in particular, at the interfaces, are not comprehensively understood. A successful approach for crystalline materials with small number densities of point defects is the space charge concept by Maier [11], assuming an increased number density of defects in the so-called space charge regions at the interfaces, which extend over a length scale of the order of the Debye length. For ion conducting glass ceramics and polymer electrolytes, however, this concept does not seem appropriate, since here the Debye length is of the order of atomic dimensions due to the high density of mobile ions. Alternatively, a high mobility of ions at the interfaces might be responsible for the conductivity enhancement effects. For these materials, more experimental information about the ion dynamics in different phases and at interfaces is clearly needed.

In this Letter, we provide new information about ionic movements in partially crystallized  $\text{LiAlSiO}_4$  glass ceramics. These glass ceramics consist of an amorphous  $\text{LiAlSiO}_4$  matrix containing nanoscale crystalline particles of the same composition. Since the glass ceramics are easy to prepare and the lithium ion conductivity depends strongly on the degree of crystallinity  $\chi$  [10], they are well suited as model systems for studying ion transport in materials with internal interfaces. Spatially resolved information about the ion transport can be obtained by means of time-domain electrostatic force spectroscopy

(TDEFS) [12]. This method was used to demonstrate the existence of two distinct dynamic processes with different activation energies in a 42% crystallized  $\text{LiAlSiO}_4$  glass ceramic [13], while only the faster of these two processes was observable in macroscopic conductivity spectra. The two processes were attributed to faster ionic movements in the glassy phase and slower ionic movements in the crystallites. The question, however, remained whether a third process exists that is related to ion dynamics at the interfaces.

Here we use TDEFS to prove the existence of a third process in  $\text{LiAlSiO}_4$  glass ceramics with 13% and 42% crystallinity. The experiments were performed with a commercial, variable-temperature atomic force microscopy (AFM) operating under ultrahigh vacuum (UHV) conditions (Omicron VT-AFM). The force sensor is a single crystalline, highly doped silicon cantilever with a resonant frequency of 300 kHz and a spring constant of 20 N/m, featuring a sharp conducting tip with an apex radius of 10 nm. The system is operated in the frequency modulation mode [14], where conservative tip-sample forces will induce a shift in the resonant frequency of the oscillating cantilever. For the preparation of the glass ceramics with 13% and 42% crystallinity we first prepared a glass sample as described in Ref. [10]. The surface roughness of this sample was reduced to about 1–2 nm (see Ref. [12]) and subsequently the sample was annealed in order to generate partial crystallization [10]. After insertion of the samples into the UHV chamber, the surfaces were shortly sputtered with an Ar ion beam in order to remove possible surface contaminations.

In Fig. 1(a) we sketch the basic idea of our TDEFS measurements on partially crystallized glass ceramics. The time evolution of the electrostatic tip-sample forces is monitored by changes in the frequency shift, after the conductive tip was biased with a preset voltage (ranging from  $-2$  to  $-4$  V). This gives a direct fingerprint of the dynamic behavior of the mobile ions in the nanoscopic subvolume penetrated by the electric field [12]. As an example Fig. 1(b) shows the frequency shift as a function of time at room temperature. To start a spectroscopic measurement the distance feedback is disabled, the tip is retracted by 2 nm, and the tip bias is applied. The relaxation curves show a sudden large negative frequency shift  $\Delta f_{\text{ultrafast}}$  due to ultrafast vibrational and electronic polarization occurring at all accessible sample temperatures. Subsequently, a slower relaxation process is monitored with time until the system has reached its saturation frequency value  $\Delta f_{\text{ultrafast}} + \Delta f_{\text{slow}}$ . This relaxation process can be fitted with a stretched exponential function [15] of the form:

$$\Delta f(t) = \Delta f_{\text{slow}}[1 - \exp(-(t/\tau)^\beta)] + \Delta f_{\text{ultrafast}} \quad (1)$$

where  $\tau$  and  $\beta$  denote the temperature-dependent relaxation time and the stretching exponent, respectively. The  $\beta$  values obtained from the fits ranged from 0.45 to 0.75.

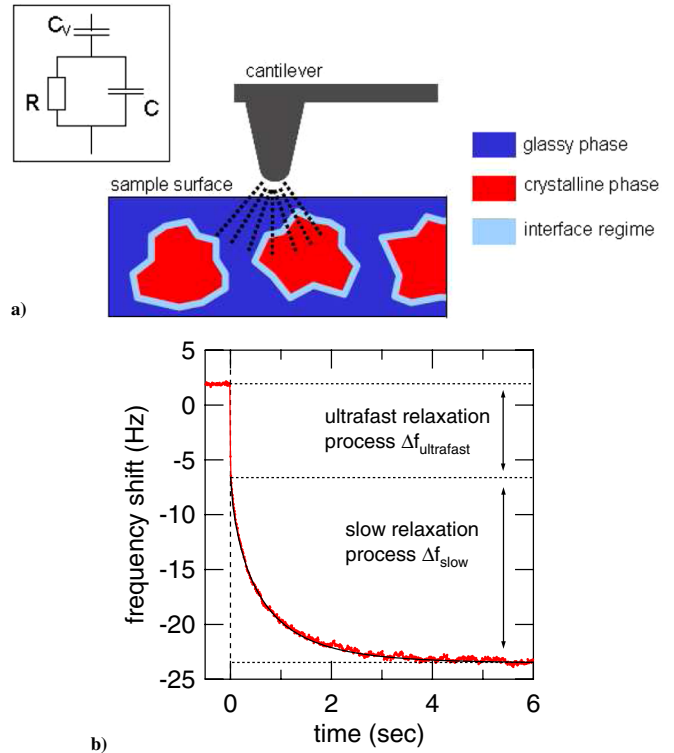


FIG. 1 (color online). (a) Schematic illustration of the principle of TDEFS measurements on partially crystallized glass ceramics. The inset shows an equivalent circuit diagram. (b) A representative relaxation curve: The frequency of the oscillating cantilever decreases with time due to attractive electrostatic tip-sample forces. In general, the curves can be divided into an ultrafast electronic and vibrational polarization process and a slow relaxation process.

The inset of Fig. 1(a) shows a simple equivalent electrical circuit diagram of an inhomogeneous ionic conductor. We assume that due to the heterogeneous structure, only a fraction of the probed volume contains ions that are mobile on the experimental time scale. This volume fraction is represented by a resistance  $R$ , which is inversely proportional to the number density of mobile ions in the probed volume  $N_V$  and to the hopping rate of the ions  $\Gamma$ . On the other hand, the entire probed volume can be electrically polarized due to ultrafast electronic and vibrational processes. This is represented by a capacitance  $C$ . We assume that this capacitance is, in a good approximation, independent of temperature.  $C_V$  is a temperature-independent vacuum capacitance due to the gap between sample and tip. In this case, the relaxation time  $\tau$  in a TDEFS measurement is given by [12]

$$\tau = R(C + C_V) \propto \frac{C + C_V}{N_V \Gamma}. \quad (2)$$

This equation implies that  $\tau$  is not simply the inverse of the ion hopping rate  $\Gamma$ , but is also strongly influenced by the number density of mobile ions in the probed volume. We note that Eq. (2) is helpful to understand the relation

between  $\tau$ ,  $N_V$ , and  $\Gamma$  on a qualitative level. However, it is important to realize that the equation contains several approximations. In particular, correlated movements of ions and a possible dependence of the effective dimensionality of the transport pathways on the degree of crystallinity are not taken into account. Therefore, Eq. (2) cannot be used to predict quantitative values for  $\tau$ .

The time window of the measurement is limited to the range from 1 ms to 10 s. Therefore we had to adjust the sample temperature such that the thermally activated jump processes of the ions are within the accessible time range. The measurements can be categorized into three temperature regimes: (a) medium temperature range (200–300 K), (b) high temperatures (above 500 K), and (c) low temperatures (below 170 K).

From macroscopic conductivity measurements [10] it is known that LiAlSiO<sub>4</sub> glass is a moderate ion conductor with an activation energy of  $E_A^{\text{glass}} = 0.72$  eV, while a completely crystallized LiAlSiO<sub>4</sub> sample [16] is a poor ionic conductor with a high activation energy of  $E_A^{\text{crystal}} = 1.07$  eV. At room temperature the macroscopic electrical relaxation times  $\tau_{\text{macro}} = R_{\text{macro}} C_{\text{macro}}$  [12] of the pure glass and of the completely crystallized ceramic are about  $10^{-2}$  and  $10^3$  s, respectively. Thus the relaxation curve at room temperature as shown in Fig. 1(b) is dominated by

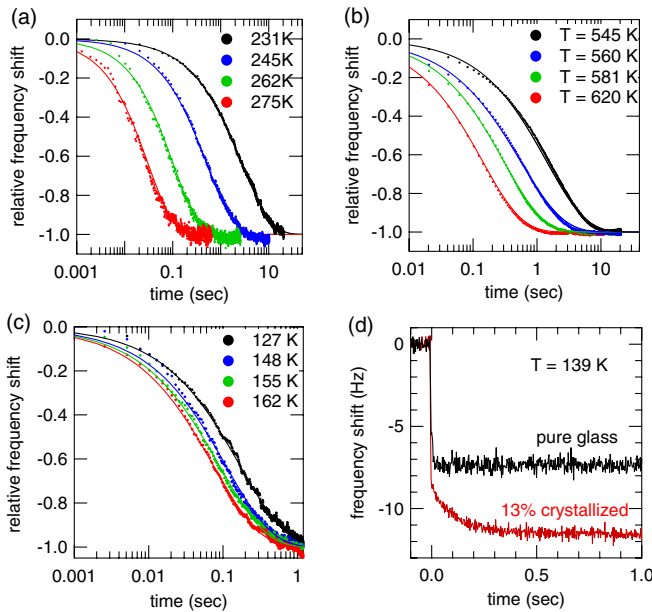


FIG. 2 (color online). TDEFS relaxation curves for a glass ceramic with 13% crystallinity in three different temperature regimes. The contributions of fast electronic and vibrational polarization are not shown, and the curves are normalized to the relaxation strength of the respective relaxation process, (a) medium temperature range (200–300 K), (b) high temperatures (above 500 K), and (c) low temperatures (below 170 K). (d) Direct comparison of relaxation curves (raw data, including fast relaxation part) under identical experimental conditions for a glass ceramic with 13% crystallinity and for a pure glass.

the contribution of the ions in the glassy phase, while the ions in the crystalline phase can be regarded as immobile with respect to the experimental time scale.

Figure 2 shows the slow part  $\Delta f_{\text{slow}}(t)$  of the relaxation curves of a glass ceramic with 13% crystallinity, which were normalized to their respective relaxation strengths for a better comparison. The logarithmic plots in Figs. 2(a) and 2(b) show the relaxation curves obtained in the temperature range from 231 to 275 K and from 545 to 620 K, respectively. The relaxation times decrease with increasing sample temperature, which corresponds to a horizontal shift of the curves to the left. A linear fit to the Arrhenius data in Fig. 3 yields activation energies of  $E_A = (0.58 \pm 0.03)$  eV and  $(1.03 \pm 0.07)$  eV. These values are in reasonable agreement with the macroscopic activation energies for a pure LiAlSiO<sub>4</sub> glass and for a completely crystallized LiAlSiO<sub>4</sub> ceramic. For comparison, previous TDEFS data for the ionic motion in the glassy phase and in the crystallites, respectively, of a glass ceramic with 42% crystallinity [13] (cross shaped markers) are shown in addition. Thus we can assign the observed relaxation processes to ion transport in the glassy phase and in the crystalline phase, respectively.

This classification is supported by the observation that the preexponential factor of the process in the glassy phase increases with increasing crystallinity, while in the crystalline phase this factor decreases with increasing crystallinity (see Fig. 3). These trends are in agreement with Eq. (2). While the activation energies of  $\tau$  and  $\Gamma$  should be identical, the preexponential factor of  $\tau$  is inversely proportional to the number density of mobile ions in the probed volume. Thus, when measuring the process in the glassy phase, an increasing degree of crystallinity should

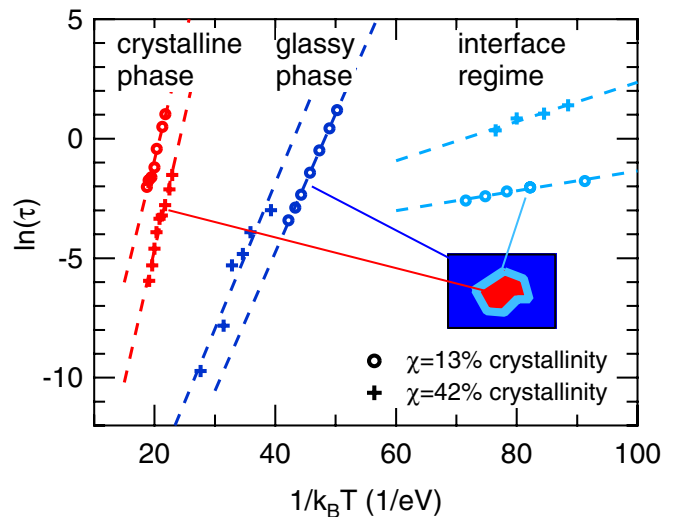


FIG. 3 (color online). Arrhenius plot of nanoscopic TDEFS relaxation times (symbols) obtained for a glass ceramic with 13% (circles) and 42% (crosses) crystallinity, respectively. The values for the activation energies obtained from Arrhenius fits of the relation times are given in the text.

lead to a decreasing number density of mobile ions, resulting in an increasing preexponential factor. Exactly the opposite trend is expected for the process in the crystalline phase, in agreement with our experimental results.

Apart from the ion dynamics observed in those two phases we find a third process, which appears in the low-temperature regime. Figure 2(c) shows relaxation curves that were obtained at temperatures from 127 to 162 K. Again, we find a systematic decrease of the relaxation times with increasing temperature, as evidenced by the horizontal shift of the curves to the left. A linear fit to the Arrhenius data in Fig. 3 yields a very low activation energy of  $E_A = (0.04 \pm 0.01)$  eV and a very large preexponential factor  $\tau_0 = 4.2$  ms. This activation energy value indicates that the dynamic process cannot be assigned to the ionic motion in the glassy nor in the crystalline phase. Therefore we suggest that this relaxation process is caused by ionic movements in the interface regime between the glass matrix and the embedded crystallites. The sizes of the crystallites are about 300 nm for 13% crystallinity and about 600 nm for 42% crystallinity [10]. Assuming that the width of the interfacial regions is of the order of a few nanometers, the number of mobile ions contributing to the interfacial process should be orders of magnitude lower than the number of ions governing the dynamics in the glassy and crystalline phase. According to Eq. (2), this should lead to a very large preexponential factor for the relaxation time of the interfacial process.

In order to exclude possible artifacts we performed additional test measurements on a pure glass sample without internal interfaces. Figure 2(d) shows representative relaxation curves of the pure glass sample and of the glass ceramic with 13% crystallinity in direct comparison at the same temperature  $T = 139$  K. While the ultrafast frequency shift due to the ubiquitous electronic and vibrational polarization is seen in both curves, only the partially crystallized sample shows a distinct relaxation process. Additionally we have performed TDEFS measurements on the 42% crystallized glass ceramic, which confirms the existence of a third relaxation process. In this case, we obtain an activation energy  $E_A = (0.08 \pm 0.01)$  eV and a preexponential factor  $\tau_0 = 2.9$  ms (see Fig. 3).

From these experimental results, the following picture about the ion transport in the partially crystalline glass ceramics emerges: The ions carry out fast hopping processes in the interfacial regions. However, since these interfacial regions do not form percolating diffusion pathways through the samples, the ions have to cross the glassy phase in order to find macroscopic diffusion pathways. Consequently, the higher activation energy for ion transport through the glassy phase governs the activation energy for macroscopic transport. On the other hand, the interfacial regions act as local electrical short circuits leading to an increase of the ionic conductivity as compared to a pure LiAlSiO<sub>4</sub> glass. If the interfacial regions were percolating,

the conductivity of the glass ceramics would be orders of magnitude higher than that of the pure glass. Such strong conductivity enhancement effects due to interfacial conduction have been observed in nanocrystalline composites [3,4].

In conclusion, our results demonstrate the existence of an electrical relaxation process in nanostructured LiAlSiO<sub>4</sub> glass ceramics with a low activation energy  $E_A$  and a large preexponential factor  $\tau_0$ . Since this relaxation process is absent in the pure LiAlSiO<sub>4</sub> glass, we suggest that the process is caused by local movements of ions at the interfaces between glassy phase and embedded crystallites. The low activation energy of the process indicates that the hopping rate of the mobile ions at the interfaces is high, while the high preexponential factor indicates a small number of ions contributing to the process.

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