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Ionic Conductivity in $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ Based Glasses and Glass Ceramics

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The complex conductivity of lithium aluminosilicate based glasses and glass-ceramics (Zerodur from Schott) has been investigated in a broad range of temperatures ($200\text{ K} < T < 700\text{ K}$) and frequencies ($10\text{ MHz} < \nu < 2.5\text{ THz}$). The data are presented in terms of the conductivity and the electrical modulus formalisms. The width of the modulus loss peak as measured for the ceramic sample is broader than that determined for its precursor glass. This result is shown to be associated with the considerably smaller dc conductivity of this material.

1. Introduction

Certain complex crystals exhibit a very small or negative coefficient of thermal volume expansion, i.e. along certain crystallographic axes they contract upon heating. The stuffed aluminosilicates β -eucryptite [1] (LiAlSiO_4) and β -spodumene ($\text{LiAlSi}_2\text{O}_6$) [2], for instance, show this remarkable behavior. The latter crystal consists of 5, 7, and 8 membered rings of SiO_4 and AlO_4 tetrahedra, and charge balancing Li^+ ions occupying half of the interstitial sites in the unit cell [3]. On heating the tetrahedral groups perform an increasing tilting, thus counterbalancing the thermal expansion due to the anharmonic lattice vibrations. In vitreous LiAlSiO_4 and $\text{LiAlSi}_2\text{O}_6$ the structural arrangement necessary to achieve these effects is strongly disturbed, and consequently these glasses exhibit the more familiar positive volume expansion on heating. Therefore glass ceramics on $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ basis, containing the appropriate fractions of glassy and crystalline phases, can be produced which exhibit extremely small expansion coefficients in selectable temperature ranges [4].

In order to manufacture homogeneous materials with well defined crystalline fractions one adds to their precursor glasses a number of oxides, predominantly (earth) alkali oxides as well as Zr and Ti oxides, the

latter ones acting as nucleation agents. Notably the alkali ions show a large mobility in the aluminosilicate host. The presence of ions such as Li^+ and Na^+ , which have quite different ionic radii, can lead to complex relaxation phenomena. Presumably the most important one is the mixed alkali effect [5]. The recognition that this effect is responsible for the obnoxious hysteresis effects observed in some glass ceramics has led to further improvements in the performance of these technologically important materials [6].

Hence it is highly desirable to study the motions of the mobile ions in this class of materials. Numerous studies deal with the ionic conductivity in the audio-frequency range in crystalline [7–9] and vitreous [10–13] aluminosilicates, but also with technologically relevant ceramic materials [13–16]. In this article we investigate the conductivity of Zerodur in a frequency range of more than 14 decades and analyze our data in various ways.

2. Experimental

The exact composition of the $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ based ceramic Zerodur is given in [17]. The conductivity measurements at lower frequencies were done on disk-shaped samples cut from the ingots. The specimens were polished, and gold electrodes were sputtered onto both faces. The complex conductivity $\sigma = \sigma' + i\sigma''$ was measured using four- ($10\text{ MHz} < \nu < 3\text{ MHz}$) and two- ($1\text{ MHz} < \nu < 10\text{ GHz}$) point contact geometries

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for temperatures $200 \text{ K} < T < 700 \text{ K}$. For the experiments in the far infrared spectral range ($68.4 \text{ GHz} < \nu < 2.522 \text{ THz}$) electromagnetic radiation of intensity I_0 was passed through wedge-shaped samples. From the transmitted intensity $I(d)$ the absorptivity α was calculated according to $\alpha = d^{-1} \ln(I_0/I)$. The sample geometries we used here allow the continuous variation of the sample thickness d at a given frequency and temperature, thus minimizing problems due to surface reflections and interference effects (due to multiple reflections). From the absorptivity the conductivity can be obtained via $\sigma'(\omega) = \epsilon_0 c n \alpha(\omega)$. Here ϵ_0 is the permittivity of free space, c the velocity of light, and n the index of refraction. The latter quantity was measured in the far infrared using Mach-Zehnder interferometers [18]. Typically n was independent of frequency in the range studied and increased linearly with temperature.

3. Results and Discussion

The conductivity of Zerodur is shown in an Arrhenius plot in Fig. 1 for a number of frequencies and also as measured under dc conditions. σ_{dc} is thermally activated, i.e. $\sigma_{\text{dc}} = \sigma_0 \exp(-E_{\text{dc}}/k_B T)$ with $\sigma_0 = 5.5 \Omega^{-1} \text{ cm}^{-1}$ and $E_{\text{dc}} = 0.90 \text{ eV}$. Under ac conditions the conductivity at a given temperature increases strongly with the measuring frequency. It is remarkable that the slope $d[\ln \sigma(\omega)]/d[1/k_B T]$, which sometimes has been called ac activation energy, $E_{\text{ac}}(\omega)$, decreases with increasing frequency. The various apparent energy barriers defined in this way are related by the empirical expression [19, 20] $E_{\text{ac}} = (1-s) E_{\text{dc}}$. Here s is an exponent which is sometimes used to parameterize the frequency dependent conductivity via $\sigma(\omega) = \sigma_{\text{dc}} + A \omega^s$ [21, 22]. Considering the decrease of the low temperature slopes $|d \ln \sigma'/d(1/T)|$ with frequency, seen in Fig. 1, one would argue that, if the empirical relation is valid, s should increase with frequency. This is indeed the case for the ceramic aluminosilicates [15]. For the precursor glass the explicit frequency dependence of the conductivity is shown in Figure 2. The frequency exponent is seen to increase from $s=0$ at the lowest frequencies (dc conductivity) [23] to a regime where $s \approx 1$. At the highest frequencies ($\nu > 100 \text{ GHz}$) the effective power law exponent is even larger than unity. In the inset we show an Arrhenius plot for the dc conductivity which can be described by $\sigma_{\text{dc}} = 0.61 \Omega^{-1} \text{ cm}^{-1} \exp(-0.67 \text{ eV}/k_B T)$.

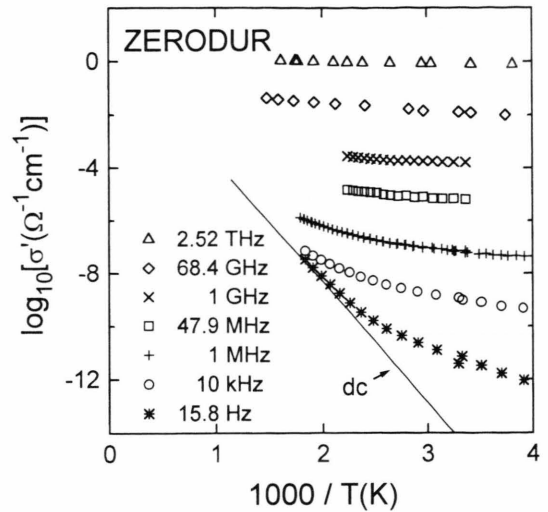


Fig. 1. Conductivity of Zerodur plotted as $\log \sigma'$ versus inverse temperature for several frequencies. The slope of the solid line represents the activation energy, $E_{\text{dc}} = 0.90 \text{ eV}$ that was obtained from dc measurements. Note that the effective low temperature slopes $|d \ln \sigma'/d(1/T)| (\propto E_{\text{ac}})$ increase with decreasing frequency.

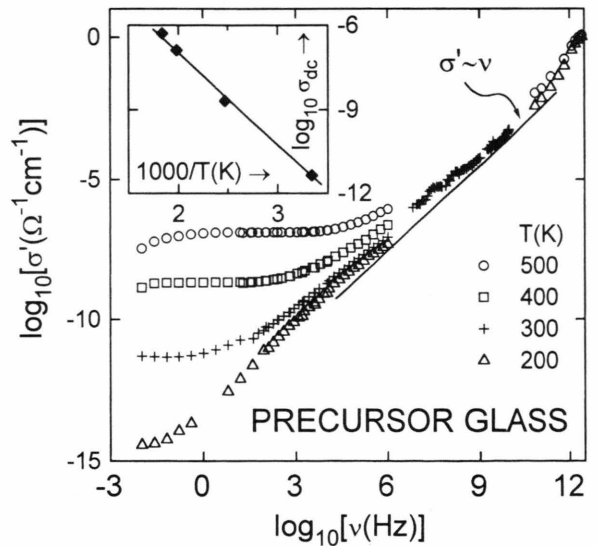


Fig. 2. Double logarithmic representation of the frequency dependent conductivity of Zerodur precursor glass. For intermediate frequencies the data follow roughly a $\sigma' \sim \nu$ dependence. At higher frequencies deviations from this simple behavior become apparent, which are due to vibrational excitations. At lower frequencies the dc plateau is seen. At high temperatures and very low frequencies deviations from the plateau behavior are clearly visible. These are due to the formation of blocking electrodes. The inset shows the dc conductivity in an Arrhenius representation.

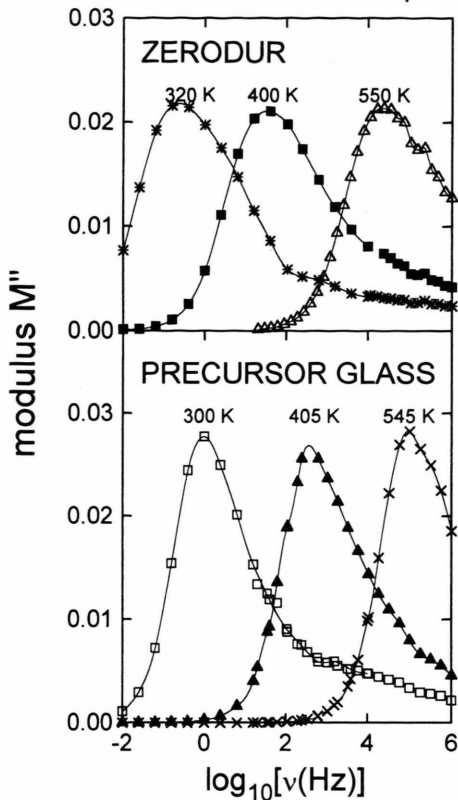


Fig. 3. Imaginary part of the electric modulus M'' of Zerodur glass and glass ceramic. The spectra of the glass ceramic are rather broad and exhibit additional contributions at high frequencies. The latter are similarly observed for the precursor glass. Lines are drawn to guide the eye.

At first glance the data shown in Fig. 2 look quite similar to those of the ceramic samples published previously [15]. The differences in the behavior of the two samples becomes more obvious in the electric modulus (M) representation [14]. The imaginary part of M , given by $M'' = \epsilon_0 \omega \sigma' / (\sigma'^2 + \sigma''^2)$, is shown in Fig. 3 for the Zerodur glass ceramic (upper frame) and its precursor glass (lower frame). For both ion conductors well defined modulus peaks are found. In addition to the main peaks, a relatively strong high-frequency wing shows up, which has previously been reported to occur also for a related $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-2\text{SiO}_2$ glass [10].

The widths of the modulus loss peaks, $M''(\log_{10} \omega)$, are significantly broader for the partly crystalline compound as compared to what is observed for the fully amorphous pendant, see Figure 3. If one associates the width of the modulus peak with the width of a distribution of conductivity relaxation times [10],

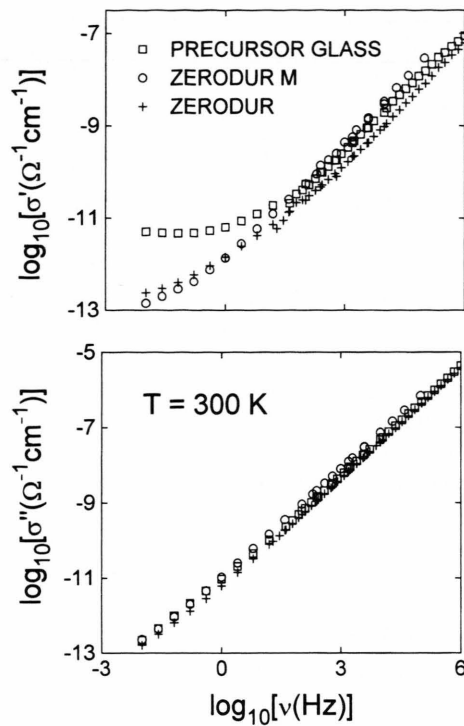


Fig. 4. Real and imaginary parts of the complex conductivities of Zerodur glass ceramics and precursor glass as measured at $T = 300$ K. Also included is a set of data taken on Zerodur M, a previously studied [16] glass ceramic with a slightly different composition. It is clearly seen in the upper frame that the precursor glass exhibits a pronounced dc plateau, in contradistinction to what can be observed for the ceramic samples.

and hence with a distribution of local environments, then the results presented in Fig. 3 suggest that the ceramic is more disordered than the glass, which is counter to what one may have expected. A different interpretation of the widths of the modulus peaks can be obtained if one accepts the above mentioned, but somewhat artificial separation of the conductivity into ac and dc components. Under this assumption one would conclude that the two contributions should appear with different weights in the different forms of the aluminosilicates.

This statement can be checked directly by comparing the complex conductivities of glassy and ceramic samples as is done in Figure 4. It is clearly seen in the upper part of this figure that the ac conductivities differ little for the various samples. However the dc conductivity in the glassy specimen, measured at room temperature, is about two orders of magnitude larger

than in the ceramic samples. Inspection of the lower part of Fig. 4, which shows $\log_{10} \sigma''$ versus $\log_{10} \nu$, reveals that all samples behave quite similarly, i.e. they exhibit similar refractive indices ($n = [\sigma''/(\omega \epsilon_0)]^{0.5}$ at high frequencies) and similar frequency exponents s (given by the low frequency slope in σ'').

The higher dc conductivity of the glassy sample is to be related to the fact that it exhibits a conduction barrier E_{dc} that is smaller than that of the ceramic material. This observation has been made in a similar manner for a number of other stuffed aluminosilicates [8, 13] and seems to be consistent with Ingram's "cluster bypass model" (CBM) [24]. Pechenik *et al.* ascribed the startling increase of E_{dc} in the ceramics to ion-correlation effects [11] which from Monte Carlo simulations were found to lead to an increase of the dc conductivity [25]. Ion correlation effects, however, may be expected to have an impact on the ac contributions as well.

Therefore it cannot be ruled out that the difference in the dc conductivities (however to a much lesser extent than in the ac conductivity) is at least partly due to differences in the Li ion concentrations in the two phases. If it is assumed that in the absence of external electrical fields charge neutrality is maintained on mesoscopic length scales, then the presence of the crystallization inducing cations (presumably immobile) in the crystalline phase would lead to an effective reduction of the concentration of the mobile charge carriers.

To carry these ideas further we draw attention to the issue of ionic decoupling which has been related to the CBM [26]. For amorphous materials the decoupling index is defined as $R = \tau_s(T_g)/\tau_\sigma(T_g)$. Here $\tau_s(T_g) \approx 100$ s is the structural (enthalpy) relaxation time at the glass transition, and the conductivity relaxation time is given by $\tau_\sigma = \epsilon_0/(M_\infty \sigma'_{\text{dc}})$ [10]. The decoupling index, $R \propto \sigma'_{\text{dc}}(T_g)$, is small for systems in which the motions of the ions freeze out at T_g . But R can be as large as 10^{15} if the ionic mobility is fully decoupled from the amorphous (network) matrix [26]. Angell has drawn attention to an empirical relation according to which the width of the modulus spectra

increases with the decoupling index [26]. While the data for the precursor glass are well within the range of this correlation [27], the decoupling index for the ceramic (evaluated at the glass temperature of the fully amorphous sample) is smaller, despite *broader* modulus spectra. Such deviations from the correlation can be expected e.g. in the presence of incipient phase separations [26] and certainly also for nano-phase separations as they are characteristic for the glass ceramics studied in this work.

4. Summary

Results from a broad-band impedance investigation of $\text{Li}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$ based glasses and glass ceramics have been reported for temperatures $200 \text{ K} < T < 700 \text{ K}$. Between the σ_{dc} -plateau and the constant loss regime (characterized by $\sigma \propto \nu$) deviations from the usual power law behavior have been found. In the electrical modulus representation of the data these deviations show up as small extra contributions (due to dipolar relaxation processes) to the high-frequency wings of the M'' peaks. The peaks were significantly broader for the ceramic as compared to the amorphous sample. Since it appears somewhat unlikely that a potential distribution of conductivity relaxation times is broader in a ceramic than in its precursor glass, the different widths were related to the different ratios of ac and dc contributions to the conductivity of both samples. We have discussed these observations in relation to the cluster bypass model. The relative broad modulus spectra of the precursor glass are consistent with the large decoupling of the Li ion motion from that of the host matrix according to the correlation suggested by Angell [26].

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