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Glassy, ceramic, and crystalline lithium aluminosilicates: charge transport and low-temperature specific heat studies

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Abstract

Using dielectric techniques in the frequency ranges from 0.01 Hz to 1 GHz and from 60 GHz to 3 THz, the transport, relaxational and vibrational motions of Li ions in stuffed aluminosilicates were studied. Samples investigated include the polycrystal β-eucryptite, the ceramics Zerodur M and Zerodur as well as the precursor glass of the latter compound. Conductivities similar in magnitude are found for all samples at high temperatures. For temperatures well below ambient, local dielectric relaxations are observed. Their appearances strongly depend on the degree of the crystallinity of the host matrix. For the Zerodur samples, the far infrared measurements yield evidence for excess absorptions at vibrational frequencies. In order to test whether these excitations are associated with an enhanced density of states, the specific heat of several aluminosilicates has been measured for temperatures between 5 and 50 K using the adiabatic Nernst method.

1. Introduction

The study of ionic motions in disordered solids is continuing to attract the attention of many researchers. This is not only because of the numerous technical applications of solid state ionics [1], but also because of the fundamental interest in understanding the microscopic transport mechanisms [2]. At high temperatures, in the molten state, the ions are characterized by a very high mobility and the relaxation rates usually follow a non-Arrhenius dependence. At lower temperatures the non-mobile ions form a crystalline or amorphous network which can provide pathways along which the decoupled (mobile) ions can be transported. Recently some consensus seems to be emerging that these processes are accompanied by *local* structural relaxations [3], leading to the notions of correlated forward–backward hopping processes [4] and site memory effects [5]. For temperatures typically far below ambient the long-range ionic transport ceases to dominate the response to externally applied electrical fields and eventually vibrational and tunneling excitations take over [6].

Some ion conducting solids, including the aluminosilicates dealt with in the present article, provide a peculiar structure which makes it possible to observe local ion relaxations in virtually fixed local structures [7]. This is because in these systems local

[1] The work of F.D. was carried out as part of a PhD. thesis at the Universität Mainz

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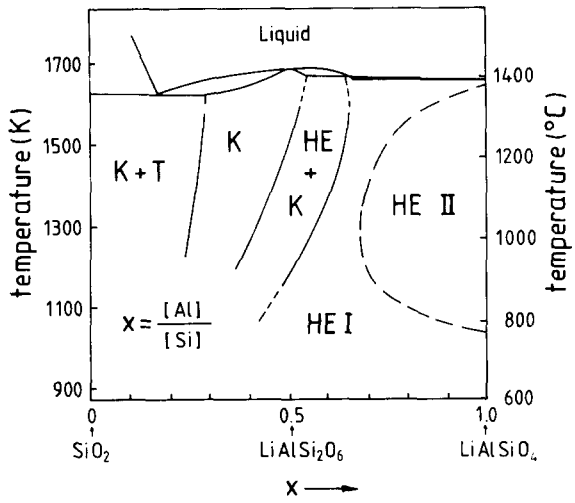

Fig. 1. Phase diagram of the binary system silica–eucryptite (SiO_2–$LiAlSiO_4$) after Roy and Osborn [10] and Hahn and Behruzi [11]. The crystallographic structures which occur in the solid solutions are the tridymite (T), keatite (K), and high eucryptite (HE) phases, the latter being characterized by disordered (I) and ordered (II) silicon/aluminium arrays. The composition of the stoichiometric compound spodumene corresponds to a concentration $x = [Al]/[Si] = 0.5$. Zerodur and Zerodur M can be characterized by [Al]/[Si] ratios of 0.52 and 0.44 respectively.

double well potentials exist with energy barriers much smaller than those which govern the long-range ion transport [8]. It can certainly be expected that the variability of those local structures will depend on the crystallinity of the samples. It is well known that in eucryptite–silica ($LiAlSiO_4$–SiO_2) based solid solutions amorphous, ceramic (microcrystalline), and crystalline modifications can readily be prepared over large composition ranges [9]. Therefore this system proves to be ideally suited for studying the interplay of long-range, localized, and vibrational ionic motions.

The (x, T) phase diagram of $LiAlSiO_4$–SiO_2 is shown in Fig. 1 [10,11]. With increasing concentration $x = [Al]/[Si]$ the fraction of Al^{3+} which substitute for the Si^{4+} ions in the SiO_4 tetrahedra requires an increasing amount of Li^+ ions to balance the charges. At $x = 0.5$ the existence of the stoichiometric compound spodumene, $LiAlSi_2O_6$, is noted. In this binary system with its complicated phase equilibria, crystals are usually prepared by recrystallization of quenched melts (glasses) at elevated temperatures. To obtain microcrystalline, ceramic samples with well defined grain sizes, small amounts of nucleation agents like ZrO_2 and TiO_2 have to be added to the melts.

In this work we have studied the long-range transport and the localized and vibrational ionic motions in Li_2O–Al_2O_3–SiO_2 based materials using broad-band impedance spectroscopy. We have also carried out complementary low-temperature heat capacity experiments. The aluminosilicates of interest here are Zerodur and Zerodur M glass-ceramics which, owing to different thermal treatments in the temperature range 600–850°C, exhibit degrees of crystallinity of 70 and 50%, respectively. In addition to these glass-ceramics, characterized by [Al]/[Si] concentrations of $x = 0.44$ (Zerodur M) and $x = 0.52$ (Zerodur), we have studied the precursor glass of the latter compound as well as polycrystalline samples of β-eucryptite ($x = 1$).

2. Experimental

The amorphous and cerammed samples of Zerodur and Zerodur M were provided by Dr W. Pannhorst from Schott Glaswerke. The crystallite fractions are $(70 \pm 3)\%$ and $(50 \pm 3)\%$ and the average grain sizes 62 nm and 45 nm, respectively. The β-eucryptite sample was produced by sintering powdered ingots. This simple method yielded a polycrystalline sample with 94% of the density of the single crystal [10]. Electron micrographs revealed average grain diameters of about 10 μm.

At frequencies $\nu = \omega/2\pi = 10^{-2}$–$10^9$ Hz and for temperatures $10\,K < T < 600\,K$ we have measured the complex conductivity, σ, of gold plated samples using the Schlumberger 1260, the HP 4284, and HP 4191 impedance analyzers in the sub-audio, audio, and radio-frequency ranges, respectively. For selected temperatures absorptivity measurements [12] were carried out at 9 frequencies in the range from 2 to $100\,cm^{-1}$ ($60\,GHz < \nu < 3\,THz$), i.e., in the far infrared (FIR). From the absorptivity, α, the conductivity was calculated according to $\sigma'(\omega) = \varepsilon_0 c n(\omega)\alpha(\omega)$. Here ε_0 is the permittivity of free space, c the velocity of light, and n the

refractive index. For Zerodur M the latter was found to be $n = 2.5$ independent of frequency in the range studied. Heat capacity measurements were conducted for temperatures 5 K < T < 50 K using an adiabatic Nernst calorimeter.

3. Results

3.1. Long range ionic transport

Fig. 2 shows the conductivity, $\log_{10} \sigma'(T)$, of Zerodur M for several audio-frequencies. Above $T \approx 200$ K the low frequency data exhibit a strong increase with temperature. At higher frequencies the increase in σ' is much less pronounced. A very interesting feature is seen in the vicinity of $T = 100$ K. Here σ' exhibits indications of frequency dependent maxima superimposed on the tails of the conductivity which dominates at higher temperatures.

A clearer impression of this low temperature behavior is gained from Fig. 3 where we have replotted the data as dielectric loss $\varepsilon'' = \sigma'/\varepsilon_0\omega$ versus temperature. The temperature at which ε'' is

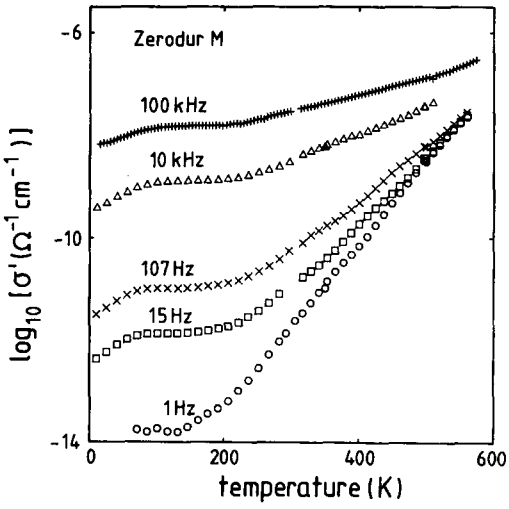

Fig. 2. Conductivity as a function of temperature as measured for the glass ceramic Zerodur M at several audio frequencies. Note the weakly developed peaks observed for temperatures in the vicinity of 100 K.

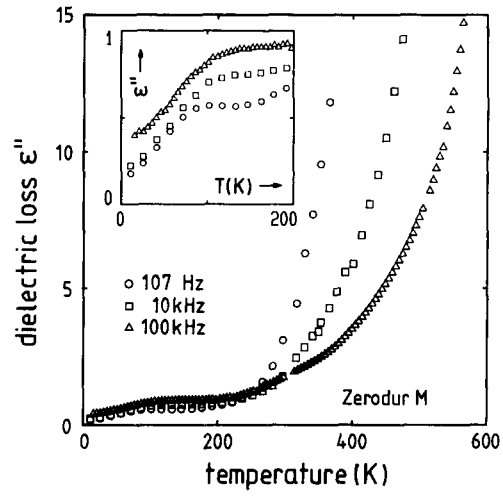

Fig. 3. Temperature dependent dielectric loss of Zerodur M. The inset is an enlargened view of the results obtained for $T < 200$ K.

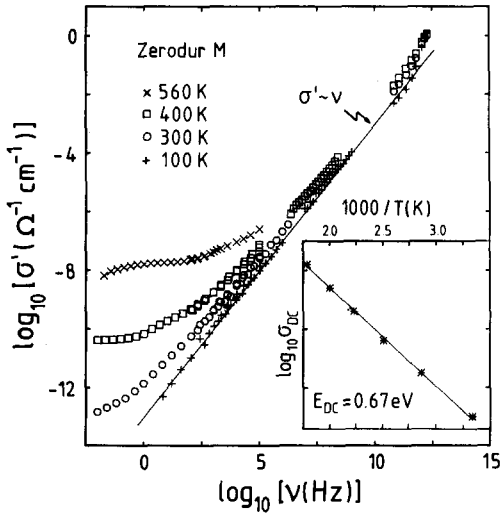

Fig. 4. Conductivity of Zerodur M plotted double-logarithmically versus the measuring frequency. The solid line represents constant loss behavior which dominates for frequencies between about 10 MHz and 600 GHz. At lower frequencies deviations from $\sigma' \sim \omega$, due to ac and dc conductivities, become apparent. The spectrum taken at 560 K is distorted for frequencies below 1 Hz. Space charges accumulating near the blocking gold electrodes lead here to a spurious decrease of σ'. The inset shows an Arrhenius plot for the dc conductivity obtained by extrapolating the measured conductivities to $\nu \to 0$. The solid line is calculated using an Arrhenius law for σ_{dc} with $E_{dc} = 0.67$ eV.

maximum increases with frequency. This is characteristic of a dielectric relaxation process. The appearance of this process varies strongly with the degree of crystallinity as will be discussed below in Section 3.2. From Fig. 3 it is evident that in Zerodur M the loss associated with the dielectric relaxation is much smaller than the conductivity loss seen above ambient temperature.

Hence in a plot of $\log_{10} \sigma'$ versus $\log_{10} \nu$, shown in Fig. 4, the dielectric relaxation feature is masked by the strong increase of the conductivity. The ac conductivity which is approximately described by a power law $\sigma' \sim \omega^s$ (with $s < 1$) dominates the middle part of the spectra. At the lowest frequencies the conductivity approaches its dc value. The temperature dependence of σ_{dc} can be parameterized by an Arrhenius law $\sigma_{dc} = \sigma_0 \exp(-E_{dc}/k_B T)$ with $E_{dc} = 0.67$ eV (see inset of Fig. 4) which can be compared to the barrier of 0.75 eV as found in Zerodur [8]. At higher frequencies the constant loss regime with $\sigma' \sim \omega$ is reached. In the far-infrared spectral range significant deviations from the power law dependences show up (see Section 3.3, below).

A much more complex charge transport and relaxation behavior has been found for polycrystalline β-eucryptite. Conductivity, $\sigma'(\nu)$, and dielectric constant, $\varepsilon'(\nu)$, of this compound are shown in Fig. 5. At high temperatures the dc plateau is clearly seen in σ'. With decreasing temperatures signatures of a series of relaxation processes, which however are barely resolved in the representation of Fig. 5, shift through the audio-frequency window. It may appear surprising that this crystalline material shows evidence for a wealth of different conduction and relaxation phenomena. We note, however, that complicated electrical impedance spectra have also been reported in previous dielectric studies on single-crystalline [13] and polycrystalline [14] β-eucryptite. In particular, our data when plotted in the modulus representation reveal the existence of a two peak structure. The microscopic assignments of the peaks has been discussed extensively in the literature [14,15].

Accordingly at lower temperatures we find indications for several distinct local relaxations. These are overlapping in temperature as well as in frequency dependent representations and are

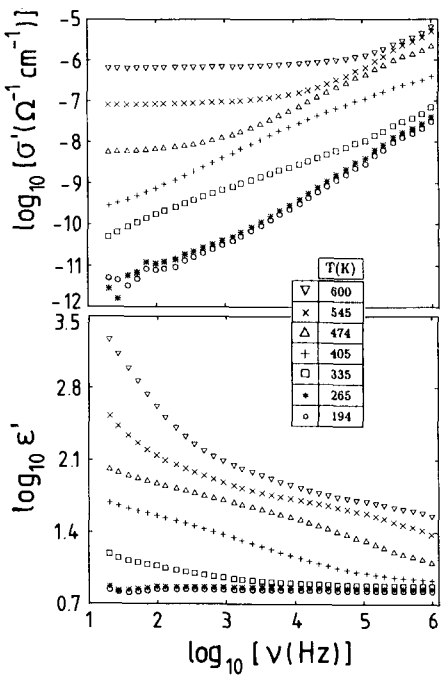

Fig. 5. Double logarithmic plot of conductivity $\sigma'(\nu)$ (upper frame) and dielectric constant $\varepsilon'(\nu)$ (lower frame) of polycrystalline β-eucryptite. At high temperatures and low frequencies pronounced dc plateaus appear in σ'. However no clear evidence for a power law behavior with $\sigma' \sim \nu^s$ can be obtained due to the occurrence of several interpenetrating conductivity and relaxation processes. The signatures of these processes are seen in the dielectric constant as several broad dispersion steps.

superimposed on a conductivity background. Hence in the following we restrict ourselves to the presentation and discussion of the results for the ceramic and glassy materials in which indications for a unique local relaxation process has been obtained.

3.2. *Local relaxations*

Most previous studies on Li-conducting aluminosilicates have focussed on investigating the cooperative ionic transport at temperatures above ambient [13–16]. As we have already seen in Fig. 3 indications for a dielectric relaxation process are obtained for Zerodur M at lower T, at which the conductivity is strongly reduced. Similar signatures of local relaxations have also been reported for

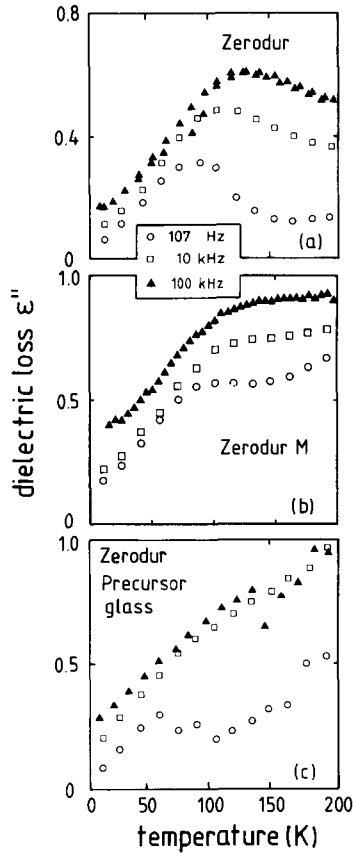

Fig. 6. Temperature-dependent dielectric loss of Zerodur ((a) 70% crystalline), Zerodur M ((b) 50% crystalline) and Zerodur precursor glass ((c) fully amorphous) as measured for several audio-frequencies. It is clearly seen that the decreasing degree of crystallinity leads to a rapid blurring of the dielectric loss peaks.

ceramic and glassy Zerodur [8] and are reproduced in Fig. 6 together with the results for Zerodur M in order to demonstrate how the appearance of the peaks changes on variation of the degree of crystallinity. In Zerodur for which the recrystallized fraction is largest (70%), the local structure can be expected to be defined better than in Zerodur M (50% crystalline) and hence should allow for a more reliable determination of the local energy barrier, E_1. While for Zerodur we find $E_1 = 0.18$ eV [8], quantitative determinations of the energy barriers in Zerodur M and in the precursor glass are not possible. However, the fact that the anomalies appear in roughly the same temperature range for all three samples suggests that the local barriers are of comparable magnitude. Particularly in the glassy sample the loss anomalies are very broad, consistent with the notion that here the local structures exhibit the largest variability.

3.3. *Vibrational excitations*

Fig. 7 shows the far-infrared absorption spectra of several aluminosilicates plotted as $\alpha(k)/k^2$, with k being the wavenumber (1 cm^{-1} corresponds to 30 GHz). This representation was chosen because the absorptivity, α, can be written as $\alpha(k) = Mg(k)$ with M being a generalized coupling constant and $g(k)$ the density of states [17]. Hence for a Debye solid with $g(k) \sim k^2$ one expects $\alpha(k)/k^2$ to be constant. Within experimental error, this is indeed found for crystalline β-eucryptite (see Fig. 7). For the ceramic and glassy samples the $\sigma' \sim \omega^s$ behavior with $s \approx 1$ leads to $\alpha/k^2 \sim k^{-s'}$ with $s' \approx 1$ as also seen in Fig. 7. However for 20 to 100 cm^{-1} deviations

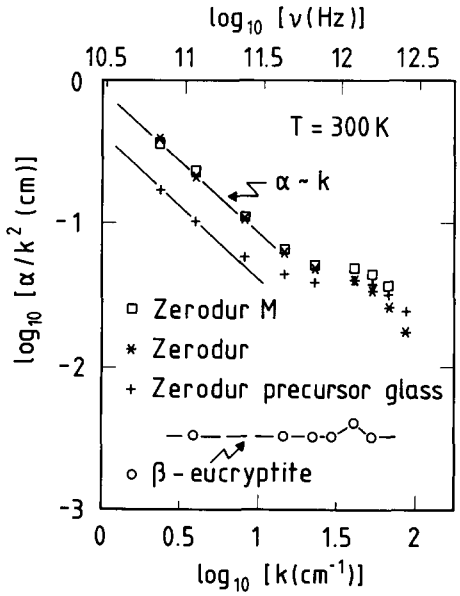

Fig. 7. Absorptivity, α, versus the wavenumber, k, for several aluminosilicates. From the excess absorptions seen in the range 40–50 cm^{-1} excess contributions to the specific heat in the temperature range from 13 to 17 K are expected.

from this power law behavior are seen as excess absorptions with maxima in the 40–50 cm^{-1} range.

4. Discussion

4.1. Long range ionic transport and local relaxations

The occurrence of local relaxations is related to a peculiarity in the structure of the aluminosilicates. It is well known that the crystalline representatives of this class of compounds, like β-eucryptite and β-spodumene, contain pairs of interstitials with the two sites in the pair being only about 1.5 Å apart [11,18]. Therefore only one Li^+ ion can occupy this double well structure at a time. The mean separation of adjacent paired sites is of the order of 4.5 Å, suggesting that the effective barriers against intrasite jumps will be much smaller than the ones that have to be surmounted during intersite hops. For Zerodur we find for instance $E_{dc}/E_l \approx 4$ [8].

It is clear that the dc activation energy essentially contains contributions from the long range Coulomb repulsions of the mobile ions. However the possibility exists that also the local freezing process is affected by the mutual electrostatic repulsions of the Li^+ ions. In that case one is inclined to predict a phenomenon which could be viewed as a 'positional' glass transition of the Li^+ ions in the structurally arrested aluminosilicate host matrix. It remains to be seen whether this phenomenon can be related to that associated with the recent observation of specific heat anomalies in Ag^+ conducting glasses in the vicinity of liquid nitrogen temperatures [19].

The occurrence of such transitions even in predominantly crystalline materials such as Zerodur should also have an impact on the low temperature thermal properties. For interacting, disordered systems, properties like the thermal conductivity and the specific heat are well known to show characteristic anomalies [20].

4.2. Vibrational excitations

In order to discuss the excess far-infrared absorptions presented in Fig. 7 we note that, in the dominant phonon approximation, vibrational modes with an energy of $3k_BT$ give rise to contributions to the constant-pressure specific heat predominantly at temperatures T, i.e., excitations at 3 cm^{-1} give rise to an enhancement of the specific heat, C_p, at about 1 K [20].

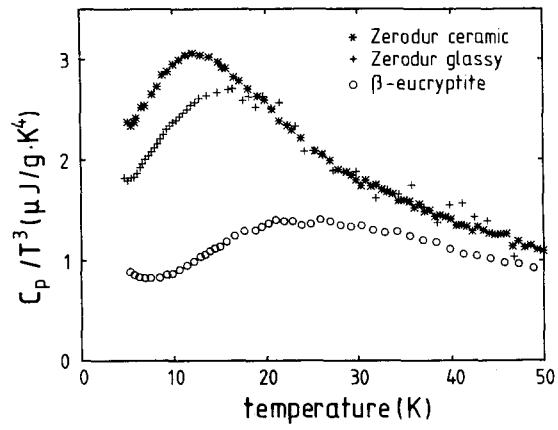

Fig. 8. Specific heat of Zerodur (*), Zerodur M (+), and β-eucryptite (○) plotted as C_p/T^3 versus temperature. The specific heats of glassy and ceramic Zerodur exhibit large excess contributions over that measured for crystalline β-eucryptite. Except for the latter compound a linear term in C_p can be expected to show up to very low temperatures. However the upturn in the data seen for $T \lesssim 6$ K may indicate the presence of traces of magnetic impurities [22].

In order to check this correspondence we have carried out specific heat measurements for 5 K < T < 50 K. In Fig. 8 the C_p data are presented as C_p/T^3 for several glassy, ceramic, and crystalline aluminosilicates. All samples show clear deviations from the simple T^3 law expected for purely harmonic solids. The data for the Zerodur samples yield maxima at $T = 12.1$ K (ceramic specimen) and $T = 17.8$ K (vitreous specimen), consistent with the FIR results [21]. The behavior of β-eucryptite expectedly is closest to that of a Debye solid. However, also in this compound excess contributions to C_p show up which may be ascribed to the disorder in the Si–Al sublattice [22].

The most striking observation made from Fig. 8 probably is that the specific heat of the more crystalline solid, Zerodur, is larger than that of its amorphous companion compound. Cahill et al. have attempted to associate this startling behavior with the random freezing of the Li^+ ions [22].

Their rationalization was suggested by the observation that some Mg^{2+} balanced precursor glasses on ceramming exhibit a *reduction* in the excess specific heat [22]. The ceramic sample investigated by these authors contains cordierite as the dominant crystal phase. The distinguishing difference as compared to eucryptite is that cordierite is a material in which the mobile ions occupy a regular array of interstitial sites.

5. Summary and conclusions

We have performed an ac conductivity study on several Li-conducting aluminosilicates. Zerodur M, a Li_2O–Al_2O_3–SiO_2 based glass ceramic with a crystallite fraction of 50%, has been investigated in a frequency range of more than 14 decades. With increasing frequencies we find evidence for dc conductivity, ac conductivity, constant loss behavior, and, in the far-infrared regime, excess absorptions due to vibrational excitations. As an additional feature we observe a dielectric relaxation due to local ion hopping processes at temperatures $T \lesssim 150$ K. These processes appear to be even more pronounced in Zerodur glass ceramic characterized by a crystallite fraction of 70%, but they are only very weakly developed in a vitreous material of identical composition. We conclude that the energy barriers governing the local relaxations are much smaller than the activation energy of $E_{dc} = 0.67$ eV which describes the dc transport in Zerodur M.

In the far-infrared regime ($2–100\ cm^{-1}$) we find experimental evidence for three different types of phenomena. In β-eucryptite the absorptivity $\alpha \sim \sigma'$ is proportional to ω^2 as expected for a crystalline solid in which the acoustic phonons dominate the density of states. Constant loss behavior is seen in the glassy and ceramic specimens. In addition excess absorptions with maxima in the $40–50\ cm^{-1}$ range show up. These can be related to anomalies in the specific heat which has been measured in the course of this work for temperatures $5\ K \lesssim T \lesssim 50$ K. In a C_p/T^3 versus T representation the thermodynamic results of the Zerodur samples exhibit clear maxima in the vicinity of 15 K. Thus from the combined investigation of aluminosilicates by calorimetry and by far infrared spectroscopy we are led to conclude that due to the enhanced density of vibrational states, the low temperature specific heats of the highly disordered materials are much larger than the ones measured for polycrystalline β-eucryptite.

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