Pressure Dependence of $T_g$ in Silicate Glasses From Electrical Impedance Measurements

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Abstract

The effect of pressure $P$ on the glass transition temperature $T_g$ has been estimated from a temperature dependence of D.C. electric conductivity in alkaline (albite, haplogranitic composition) and alkaline earth (anorthite) silicate and silica glasses having. Below $T_g$, the activation energy of the D.C. electrical conductivity is less than that at $T > T_g$. The inflection point on the Arrhenius dependency of the D. C. electrical conductivity as a function of $1/T$ defines $T_g$. The D.C. conductivity has been estimated from the electrical impedance spectroscopy in the frequency range 100 kHz - 0.01 Hz using parallel plate and concentric cylinder capacitor cell geometries. The electrical impedance measurements have been performed in a controlled atmospheric furnace and in three types of high-pressure apparatuses: piston-cylinder, belt and multi-anvil presses. The $T_g$ in anorthite glass varies with pressure as $T_g = 848^\circ C + 5.3^\circ /GPa \cdot P$ ($P$ is in GPa), in albite as $T_g = 688^\circ C - 9.4^\circ /GPa \cdot P$, in haplogranitic glass as $T_g = 777^\circ C - 45^\circ /GPa \cdot P$, and in silica glass as $T_g = 1050^\circ C + 50^\circ /GPa \cdot P$. $dT_g/dP$ decreases with the pressure and the contrast between activation energies of the electrical conductivity below and above $T_g$ is smeared out. Dielectric relaxation times calculated from the imaginary component of the dielectric modulus are several orders of magnitude smaller than structural relaxation times at $T_g$ and become slower with increasing pressure. The activation energy of the dielectric relaxation of silica glass above $T_g$ is equal to the activation energy of the structural relaxation. In albite glass, this activation energy correlates to the activation energy of the Na tracer diffusion coefficient. In sodium bearing glasses, $T_g$ estimated from electrical conductivity is a "sodium ion mobility" $T_g^{Na}$, corresponding to the temperature range of the overlapped $\alpha$ and $\beta$-relaxation processes and, is, therefore, shifted to lower temperatures in comparison with calorimetric and dilatometric $T_g$ measurements. The activation energy of dielectric relaxation in anorthite increases with pressure having an activation volume of $+10\pm5 cm^3/mol$, and in albite glass the activation volume is smaller and negative $-6.5\pm2 cm^3/mol$. Qualitatively, the pressure dependence of $T_g$ in silicate glasses correlates with a pressure dependence of the shear viscosity, and, thus, the measurements of pressure dependence of $T_g$ provide an indirect information of the melt rheology under pressure.

Key word: glass transition, pressure, impedance spectroscopy, silica, albite, anorthite, haplogranite
**Introduction**

**Pressure Dependence of Viscosity and \( T_g \)**

The glass transition temperature \( T_g \) of silicates is isoviscous temperature at which melts believed to possess a viscosity \( \text{c. } 10^{12-13} \) Pa s and a relaxation time of shear stress is about 100 s [1].

Knowledge of the glass transition temperature at high pressures provides an indirect information about the pressure dependent rheology and the effect of glass densification on relaxation processes. This is of special interest in geosciences and in silicate melt physics, where the viscosity measurements at high pressures and temperatures are technically difficult to carry out while *in-situ* rheological measurements require X-ray radiography and synchrotron radiation technique [2].

The pressure dependence of silicate melt viscosities at high pressures plays a key role in the prediction of accumulation of partial melts in mid-oceanic regions and magma accent to the Earth’s surface [3]. For decades earth scientists have sought a general equation to model the viscosity of magmatic silicate melts as a function of temperature, pressure and composition (see, for example [4-8]). In early viscosity models [4, 5], the Arrhenian temperature dependence of viscosity

\[
\log \eta_T = A + \frac{\Delta E_a}{RT} \tag{1}
\]

was suggested, where \( \Delta E_a \) is the activation energy of viscous flow, \( A \) is pre-exponential factor, \( R \) is the universal gas constant. Eq 1 exploits two parameters both of which depend on melt composition. In [5] the number of fitting parameters in Eq 1 has been reduced to \( \Delta E_a \) (\( A \) was assumed equal to -3.5 for all substances) making the use of this viscosity model highly unpractical. Recent experimental results demonstrate that Eq 1 is not adequate for most silicate melts over a wide temperature range [6, 7]. In recent years some new models of viscosity have been applied to silicate melts by the use of VFT (Vogel-Fulcher-Tammann) equation instead of the Arrhenius type

\[
\log \eta_T = A + \frac{B}{T - T_o} \tag{2}
\]

[7, 8], or on the basis of the WLF (Williams-Landel-Ferry) equation, where the three constants \( A, B \) and \( T_o \) in Eq 2 are replaced to \( A=\log \eta_{T_g}, B=B^* (T_g - T) \) and \( T_0=(T_g - T^*) \), respectively [6]. In Eqs 1-2, \( \eta_T \) is the viscosity at temperature \( T \), and \( A, B, T_o \) are the empirical constants. In a modified form of
Eq 2 \( \log \eta_{T_g} \) is the viscosity at the glass transition temperature \( T_g \). In contrast to the temperature dependence, the pressure dependence of magmatic melt viscosity is poorly constrained. There have been few attempts to generalise the viscosity dependence on pressure: (1) either by introducing a pressure dependent activation energy in Eq 1 [5], or (2) by applying a modified form of Eq 2, a WLF-type equation, and correcting the glass transition temperature \( T_g(P) \) for pressure [6]. One unclear point in the latter approach concerns the type of glass transition temperature to be used in \( T_g \)-dependent constants \( B \) and \( T_0 \): rheological, calorimetric, dilatometric etc.? A second unclear point in a WLF-type of equation is the dependence of \( T_g \) on cooling rate \( q \), which has to be taken into account by measuring \( T_g \) from different probing methods. What method of \( T_g \) estimation is relevant to be used, cooling-heating temperature scans in a time domain or dynamic measurements in a frequency domain? The general dependence of \( T_g \) as a function of cooling rate \( q \), is as follows

\[
\frac{d \ln[q]}{dT_g} = \frac{\Delta E}{RT_g^2}
\]  

(3)

where \( \Delta E \) is the activation energy of a physical property used for detecting \( T_g \) [9, 10]. Thus, for samples with differing thermal histories, one may expect differing unrelaxed states of the supercooled melt at \( T_g \) and the uncertainty in viscosity estimations by applying the \( T_g \)-dependent constants in Eq 2 may be large. In any case, the essential part of the systematics between viscosity and pressure may be experimental or theoretical estimations of a glass transition temperature as a function of pressure for samples having the same \( q \).

A general way to describe the pressure dependence of \( T_g(P) \) is to modify Eq 3 by correcting \( \Delta E \) at normal pressure (superscript index 1) for some pressure-volume effect

\[
T_g(P) = T_g^1 \left[ 1 + \frac{P \Delta V}{\Delta E^1} \right]
\]  

(4)

or

\[
\frac{dT_g}{dP} = T_g^1 \cdot \frac{\Delta V}{\Delta E^1}
\]  

(5)

where \( \Delta V \) is the activation volume of a physical property used to determine \( T_g \) and index 1 refers to
A different approach was suggested by considering the glass transition as a second-order phase transition. In this case, a Clayperon slope of $T_s$ with pressure must obey

$$\frac{dT_s}{dP} = \frac{\Delta \beta_T}{\Delta \alpha_p} \quad (6),$$

and

$$\frac{dT_s}{dP} = \frac{T \cdot V \cdot \Delta \alpha_p}{\Delta C_p} \quad (7),$$

where $\Delta \beta_T$ is the change of the isothermal compressibilities, and $\Delta \alpha_p$ is the change of isobaric expansivities, and $\Delta C_p$ is the difference in the isobaric heat capacity between liquid and glass [12-15]. Combination of Eqs 6 and 7 (two Ehrenfest equations) provides a so-called Prigogine-Defay ratio, $\Pi$

$$\Pi = \frac{\Delta C_p \cdot \Delta \beta_T}{T_s \cdot V \cdot \Delta \alpha_p} = 1 \quad (8).$$

A number of experiments have been done on polymers, low temperature glass-formers, and silicates to test the validity of Eq 6-8 [12, 16-19]. Usually, the value of the PD-ratio, $\Pi$, is much greater than 1 ($\Pi$~ varies from 2 to 5). This violation has been explained due to the non-equilibrium nature of the glass transition [20] where one ‘ordering parameter’ does not adequately describe a phase transformation. In some works, this problem was solved by introducing an additional ‘ordering parameter’ to generalise the Ehrenfest equations for the case of the glass transition (e.g. [20, 21]).

In many studies of the glass transition, it has been demonstrated that the first Ehrenfest equation (Eq 6) may be satisfied automatically by a proper calculation procedure of the volume derivatives in respect to pressure and temperature [13, 14]. In the derivation of the second Ehrenfest equation the free Gibbs energy $\Delta G$ must be corrected to the effect of the configurational entropy $-T_e \times \Delta S_{conf}$, where $T_e > T$ an effective temperature at which processes related to the configurational entropy are “thermalized” [14]. In this way, the correctly calculated PD-ratio may be very close to 1 for some glass-formers.
Alternatively to the thermodynamic approach mentioned above, there has been an attempt to
describe the pressure dependence of the glass transition by use of the VFT relation (Eq 2) and
replacing the temperature $T$ by a pressure variable $P$. If $\tau$ is the shear stress relaxation time, which
relates to the relaxed shear viscosity as $\tau \sim \eta/G$ ($G$ is unrelaxed shear modulus), then

$$\tau = \tau_0 \cdot \exp \left( \frac{B}{P_0 - P} \right) \quad \text{at } T = \text{const} \quad (9),$$

derived from a free-volume model (e.g. [22]). By analogy with temperature glass transition, the
pressure glass transition is characterised by a pressure $P_g$, at which the relaxation time is $10^2$ s and
$P_o$ is an ideal glass transition pressure at which the viscosity exponentially diverges, (by analogy
with $T_o$ in Eq 2), $\tau_o$ denotes the relaxation time at normal pressure 0.1 MPa. In some isothermal
experiments, this behaviour of the viscosity was observed [23, 24]. On the basis of the isothermal
dielectric relaxation time measurements on supercooled strong liquids another expression was
suggested, where the parameter $B$ in Eq 9 is $\propto P$ [22]. The general expression of the relaxation time
(or viscosity) can be considered in this case in the form of Eq 2 where $B$ and $T_0$ are linear functions
of pressure [25-26]. Eq 2 or VFT-equation in this extended form has been tested on specific heat
spectroscopic measurements (enthalpy relaxation) with unsatisfactory results for fragile glass-
formers [25]. The failure of the universal pressure-temperature superposition principle is explained
by the fact that the glass transition is considered as a simple volume-activated process ($\ln \tau \sim -1/V_f$
and $V_f$ is free volume). The free volume in this approach is believed to depend on pressure and
temperature in the same way through constant compressibility and thermal expansion coefficient.
This is not true for many classes of glass-forming materials such organic glass-formers, the free
volume $V_f$ is not a linear function of pressure. Contrary results were obtained for the dielectric
relaxation of epoxy resin, where relaxation times are suitably described by the extended VFT-
equation, i.e. Eq 2 with the linear dependence of the constants $B$ and $T_0$ on pressure [22]. In order
to construct an expression for viscosity of magmatic silicate melts according to an extended form of
Eq 2 taking into account a linear dependence of $B$ and $T_0$ on pressure, we would require five fitting
parameters (two constants for the linear pressure dependence of $B$, two constants for pressure
dependence $T_0$ and a constant $A$) obtained from a large number of relaxation experiments at
different pressures and temperatures. According to a modified Eq 2 in a form of the WLF-equation,
we need only three fitting parameters and independent data on $T_g(P)$. 
Another important glass parameter needed for characterisation of glass-formers is the fragility index $m$, which represents the extent of the liquid’s deviation from Arrhenian behaviour and can be defined as follows

$$
\frac{m}{2.303} = \frac{1}{d(T_g / T)} \left[ \frac{d \ln \tau}{dT} \right]_{T=T_g} = \left[ \frac{d \log(\eta)}{dT} \right]_{T=T_g} \quad (10),
$$

where $T_o < T_g$. If a modified form of Eq 2, a WLF-equation, is used for the viscosity model, then

$$
m = \frac{1}{2.303} \cdot \frac{T_g \cdot B}{(T_g - T_o)^2} \quad (11),
$$

where $T_o < T_g$. If $dT_g/dP$ is negative, then $m$ increases with pressure and a liquid is more fragile. Contrary to conclusions obtained by using Eq 12, the viscosity model described by a modified Eq 2, predicts an increase or decrease of the fragility index $m$ directly proportional to the pressure dependence of $T_g$. This simply means that the modified Eq 2 (WLF-equation) and Eq 12 may only be applicable if the fragility parameter $m$ is small, i.e. for very strong liquids ($T_g >> T_o$) in which the divergence temperature $T_o$ is far away from $T_g$.

The relaxation model of Avramov [28] based on the entropy description of the glass transition predicts viscosity and structural relaxations as a function of pressure and temperature. According to the configurational entropy theory of Adam and Gibbs, transport processes in liquid state occurs via rearrangements of structural clusters or subunits. The entropy of this units to rearrange is a minimum configurational entropy. The rearrangement probability of structural subunits is an exponentially decaying function of the free energy barrier to rearrangement divided by a minimum configurational entropy of the cooperatively rearranging cluster $S_{conf}(T)$ and absolute
temperature $T$. Both of them, free energy barrier and configurational entropy, can be, in principle, pressure dependent. The model of [28] assumes a Poisson distribution of the Adams-Gibbs energy barriers of jump frequencies at $T_g$, with a dispersity factor exponentially proportional to the excess of the configurational entropy relative to a reference state [28]. The temperature and pressure dependence of the relaxation time $\tau$ in the frame of this phenomenological theory is as follows

$$\tau = \tau_0 \cdot \exp \left\{ \varepsilon \cdot \left( \frac{T_g}{T} \right)^a \cdot \left( 1 + \frac{P}{P^*} \right)^b \right\} \quad (13),$$

where $\varepsilon = \Delta E / PT_g$ is the dimensionless activation energy at $T_g$ ($\sim 30.5$ for silicate glasses), $a$ plays a role of a fragile parameter, $b$ is the dimensionless constant which depends on the coordination number $Z$ of the liquid lattice, $P^*$ is the pressure constant estimated from an empirical relationship of the thermal expansion coefficient $\kappa$ upon pressure $\kappa = \kappa_0 \cdot \left( 1 + \frac{P}{P^*} \right)^{-\delta}$ [29]. By introducing a pressure dependence of the coordination number $Z$, Eq 13 demonstrates a good agreement with experimental results on some polymers glass formers. After a substitution of Eq 13 in Eq 10 and neglecting the pressure dependence of constants $a$, $b$ and $C_p$, the fragility index $m$ depends on pressure as follows

$$m = \frac{\varepsilon \cdot \left( 1 + \frac{P}{P^*} \right)^b}{2.303} \cdot \left[ a - \frac{b \cdot T_g}{(P + P^*)} \cdot \left( \frac{dT}{dP} \right)_{T=T_g} \right] \quad (14).$$

Thus, depending on the sign of pressure dependence of $T_g$, the fragility index $m$ may increase or decrease with pressure. In other words, the densification of glass under pressure and fragility index $m$ are correlated via Eq 14. In fact, such a correlation simply reflects the sensitivity of $T_d / T_g$ variation in respect to pressure $P$.

The main purpose of this paper is to examine the pressure dependence $T_g$ obtained from dielectric spectroscopy measurements at high pressures on silicate glasses having differing fragility indices $m$ and coupling between viscous and dielectric relaxations. In this work estimations of Tg in some silicate glasses have done by the use of the bulk (D. C.) electric conductivity measurements under pressure.
Estimation of $T_g$ From Electrical Impedance Spectroscopy

The electrical conductivity was used as a probing tool to detect $T_g$ at high pressures. To estimate a glass transition temperature at pressure, we have used a method of defining the activation energy of bulk electrical impedance (or conductivity) in the glass transition temperature range. Despite a "decoupling" of the macroscopic viscosity and its relaxation time from electrical conductivity relaxation, the kink in a slope of the D. C. electrical conductivity plotted as function of $I/T$ can be used as an indicator of $T_g$ [30, 31]. For glasses with weakly coupled viscous and dielectric relaxation, the Arrhenius dependence of the AC-conductivity (measurements of the electrical conductivity at a constant frequency), shows two inflection points, below and at $T_g$ [30]. The inflection point below $T_g$ is frequency dependent and is due to a frequency effect when the experimental time approaching the Na-hopping time. It can be seen only for AC-conductivity curves and mostly for glasses with the weakly coupled viscous and dielectric relaxations, for example a sodium trisilicate [30, 32]. In fact, when DC-conductivity data is used, the Arrhenius plot has only one inflection point corresponding to $T_g$ [32]. For strongly couples glasses, like SiO$_2$ and anorthite, the first inflection point during heating is at $T_g$, the "instrumental" inflection points on AC-conductivity curves are at $T>T_g$ above glass transition. In [30] the author argued that the inflection point of electrical conductivity and Na-tracer diffusion data at $T_g$, result from the duration of experiments approaching the structural relaxation time. According to [33], the electric transport processes in alkaline or weakly coupled glasses consist of (1) a local charge separation or dipole electric formation/reorientation (i.e. local displacement of Na$^+$ in polar units near a non-bridging oxygen), (2) a translation motion of Na between adjacent polar units, and (3) a long range translational motion of Na between structural positions like a Frenkel point defect. The first two processes occur around the same or neighbour oxygens with a low activation energy giving a rise to dielectric losses and polarisation and not correlating with a diffusion process of alkalis. The third process occurs in a length scale between two non-bridging oxygen/sodium sites and correlates with an alkaline tracer diffusion in the case, when these sites are the nearest and the cooperativity of the charge transport is absent [34]. In strongly coupled glasses (SiO$_2$, anorthite) where alkalis are at the dilute limit the contribution to the electric conductivity is only from the latter process. In the case of albite or in other aluminosilicate glasses where the number of non-bridging oxygens is 0, the polar units formed by Na and an oxygen atom participating in AlO$_4$ unit.
The interpretation of the inflection points on D.C. conductivity curves at $T\sim T_g$ is given in [30, 35]. Electrical conductivity is always associated with a mobility of “loose” particles (alkaline atoms or impurities) whose ability to self-diffusion or polarisation is higher than other species in the structure. The essential thing for this mobility decoupling is that these “loose” particles represent always a smaller subset of the structure, i.e. the transport of this particles does not influence the structural relaxation ($\alpha$-relaxation) at $T<T_g$. Thus below $T_g$ the slope of conductivity determined by a free energy barrier for $Na^+$ and not for oxygen or $Si$ atoms, in case of sodium silicates. At $T>T_g$ the matrix itself starts to relax, the mean squared displacements of oxygen atoms $<r^2>$ become significant and this results in an increase of the energy barrier for $Na^+$ transport (conductivity or diffusion). Such a change is detected as an increase of slope of D.C. electrical conductivity in an Arrhenian plot at $T\sim T_g$ [30, 31, 35]. The detected $T_g$ is a”cation glass temperature” [35], it depends on the relative abundance of non-bridging oxygen’s, alkalis and $Q_n$ species [34]. Many recent works on the structure of $Na$-silicates and $Na$-aluminosilicates with varying ratio of $Al_2O_3/Na_2O$ [34, 36], demonstrated a non homogeneous distribution of alkalis - non-bridging oxygens pairs (channelling) and clustering of $AlO_4$- groups in three dimensional structures. The inflection point at $T_g$ on conductivity and diffusion curves, in this microsegregated structures, can be understand as a starting temperature of smoothing of channel and cluster boundaries. The transport of alkalis below $T_g$ is believed to occur predominantly along those pathways where alkalis, non-bridging oxygens and/or $AlO_4$-groups are microsegregated, and this serves a physical background for a non-Fickian diffusion and a compositional dependence of a Haven coefficient accounting a cross correlation effect of diffusion at non dilute limit of diffusing species [37].

Experiments

Description of Glass Samples

The impedance measurements were performed on glass samples of anorthite ($CaAl_2Si_2O_8$), albite ($NaAlSi_3O_8$), $SiO_2$, a haplo-granite (HPG8) composition and $SiO_2$. Compositions of silicate glass samples that were used in impedance spectroscopy experiments are listed in Table 1. In the present study we have compared the pressure dependence of $T_g$ for four different glasses. Their fragility index $m$ calculated according to Eq 10 is shown in Fig. 1. Besides the differing fragility index $m$ and plots of viscosity vs. $T/T_g$ in a spirit of the Angell classification (e. g. [38], these glasses have
very different structures and mechanisms of the electrical conductivity. They can be classified as “loose” (albite and haplo-granitic glasses), “tight” and “fragile” (anorthite), and “tight” and “strong” (SiO$_2$) conducting glasses [35], accordingly. The relationship between mechanisms of electric conductivity, dispersion, polarisation, glass transition and “mobile ion $T_g$” of these glasses will be discussed below.

The samples of anorthite and albite glass were taken from the collection of silicate glasses used by Prof. M. Rosenhauer (Göttingen), the sample of HPG8 was provided by Prof. D. Dingwell (München), and the sample of SiO$_2$ glass is a commercial glass Suprasil 300 (Heraeus, Germany), containing < 1 ppm of OH$. In SiO$_2$ the concentration of Na$^+$ is at the dilute limit. The synthetic haplo-granitic composition (HPG8) corresponds to the eutectic composition of SiO$_2$-NaAlSi$_3$O$_8$-KAlSi$_3$O$_8$ at 0.1 GPa P$_{H_2O}$ and models well a calcium-free granite system. The interest of using the HPG8 sample in the present experiments is that many physical properties of this glass have been measured in recent years [40]. The difference in physical properties of this glass and albite may be attributed to a mix-alkaline effect when a fraction of non-bridging oxygens in the structure is about 0.

**Impedance Spectroscopy Measurements**

Electrical impedance measurements were carried out using a Solartron™ 1260 Phase-Gain-Analyser interfaced with a PC. The device permits a single sine drive and analysis of a system under test over the frequency range 10µHz to 32 MHz. In the high-pressure experiments we applied a 1 V sine signal over the frequency range 0.01 Hz to 100 kHz. Typically, the frequency scan utilised logarithmic steps of 0.2 - 0.5. Signals at higher frequencies were affected by cable impedance, and at lower frequency signals became too noisy. The estimation of the “bulk” electrical conductivity from frequency scans provide a “true” dc conductivity data, and, therefore, the artefact due to a mismatch of the probe frequency and material relaxation times can be avoided [30, 32].

**Measurements at 0.1 MPa**

For measurements in the atmospheric furnace (Fig. 2), glass samples (diameter D = 6 mm, 8 mm for silica glass) were drilled out of blocks of glass and cut into discs with thickness L = 1 - 1.5 mm. Flat surfaces were polished with 0.05µ alumina powder to optical quality of the surface. The
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A sample of silica glass was polished down to 0.5 mm thickness. Pt electrodes (thickness = 5\( \mu \)) were sputtered onto both flat surfaces of the glass discs (spot diameter 4.85 mm). On the silica sample, the electrodes were sputtered with a spot of 8 mm in diameter. The samples were mounted in the inductive furnace (Heraeus\textsuperscript{TM}, Hanau, Germany) with the heating element made of Pt-wire. During the measurements, samples were fixed between alumina rods (Frialit-Degussit\textsuperscript{TM} with flat electrodes made from Pt-foil. The elongation of the sample was measured with a micrometer gauge having a precision of 0.001 mm. Electrical contact between Pt-foil and sputtered electrodes was provided by a light flat spring acting axially through one of the alumina rods. The heating rate of the furnace was approximately 20\(^{\circ}/\)h. A type S thermocouple (Pt-PtRh\textsubscript{10}) touched the Pt-foil which was in direct contact with the sample. Electrical impedance measurements were done only once on each sample during heating cycle. The geometric factor of samples \( G = \pi D^2/4L \), for albite, anorthite and HPG8 ranged from 1 to 1.3 cm, and for silica glass was approximately 10 cm. Temperature was measured and controlled using a Eurotherm\textsuperscript{TM} 818P.

**Measurements in Piston Cylinder apparatus**

For the moderate pressure experiments (0.3-1 GPa), a conventional piston-cylinder apparatus with an end load was used. The measurements of the electrical impedance were performed at pressures up to 1 GPa and temperatures up to 1200\(^{\circ}\)C (see [41] for details). The press (max. load ca. 220 tonnes) consists of two independent hydraulic cylinders: the first provides an end-load and the second moves the piston at the sample assembly. The diameter of the high-pressure autoclave is ½” (Danfoss\textsuperscript{TM}, Denmark). The inner part of a high-pressure cell is shown in Fig. 3. The pressure calibration of the cell was determined using some standard point materials: at room temperature the transformations Bi I-II-III at 2.56 GPa and 2.7 GPa were used; at high temperature, melting curves of NaCl and CsCl and the \( \alpha-\beta \) transition in LiNaSO\textsubscript{4} were used as standard points [41]. Melting points of NaCl and CsCl as a function of pressure up to 2.5 GPa has been determined \textit{in-situ} by electrical conductivity measurements. At the melting point, the observed drop in the electrical impedance at 1 kHz was ca. 2 orders of magnitude. The pressure calibration is believed to be within an accuracy of \( \pm 0.03 \) GPa. The temperature gradient in the cell has been estimated on dummy samples of pressed Al\textsubscript{2}O\textsubscript{3} powder by monitoring three separate thermocouples. We estimate a radial temperature gradient of ca. 1°/mm, and a vertical temperature gradient of ca. 2°/mm in the temperature range up to 900\(^{\circ}\)C.
A cell for electrical impedance measurements in the piston cylinder utilised a coaxial cylindrical capacitor with a geometric factor of 7-8 cm filled with the sample under test. The exact geometric factor $G$ of the cell was evaluated independently from calibration measurements on NaCl solutions (0.01M - 3 M) at 22°C and atmospheric pressure. For these purposes, a cylindrical gap between two Pt-electrodes (made of two Pt-tube 0.1 mm in thickness with outer diameters 2.2 and 4 mm) has been filled with a NaCl-solution of a known molar concentration. The measured conductivity of NaCl-solutions was compared with table values. The difference between the calculated geometric factor of a cylindrical capacitor

$$G = 2\pi \frac{L}{\ln \left( \frac{D}{d} \right)}$$  \hspace{1cm} (15),

and the measured geometric factor was about 25%, where $D$ is the diameter of an outer electrode, $d$ is the diameter of an inner electrode, $L$ is the length of the cylinder. Measurements of the geometric factor of the cell after high-pressure experiments revealed that due to the cell deformation under pressure $L$ increases by ~3-4%, $D$ increases by 1-2%, and $d$ remains constant. Overall, these variations of the cell dimensions did not affect the results of $T_g$ or dielectric relaxation measurements.

During impedance measurements in the piston-cylinder, the mass of press was isolated from the ground of the Solartron™ 1260. Wires from the Pt-thermocouple and the mass of the high-pressure autoclave were used to connect the measuring device and the cell electrodes. Before doing the high-pressure experiments a measuring cell was calibrated for short-circuit and open-circuit impedances over the frequency range 1 MHz - 0.01 Hz. A typical AC-resistance of the cell to a short connection was 0.4 Ω. These calibrations have been taken into account in the final calculations of the electrical impedance as a function of frequency. At high pressure and temperature the measurements of the electrical impedance were conducted without an automatic temperature control in order to reduce the electrical noise produced from the heater regulation. During electrical conductivity measurements, the Eurotherm™ 818P controller was switched off, and the temperature was regulated manually through a variable transformer.
Experiments in Belt Apparatus and Multianvil Press

A detailed description of the belt-apparatus can be found elsewhere [42]. The construction of the experimental cells for belt- (Fig. 4) and multi-anvil apparatus (Fig. 5) has the same principle used in [43]. The geometry of the cell was a parallel-plate capacitor with a geometric factor approximately 0.3 cm. Metallic electrodes were made from Mo-foil. The cell is protected from electrical noise of the graphite (belt-apparatus) or LaCrO$_3$ (multi-anvil press) heater by a grounded shield of Mo-foil. During the electrical impedance measurements in both apparatus the automatic temperature control was switched off. The temperature was regulated manually through a power thyristor.

D.C. Electric Conductivity From Impedance Scans

On each sample the electrical conductivity was measured only during a single heating cycle. In both configurations, one of the thermocouple wires was connected to one electrode of the cell with the AC-bridge. During the frequency scan the temperature indicator was disconnected from the thermocouple in order to avoid coupling of the two devices at low frequencies.

For each glass sample, we measured the impedance over the frequency range $f$ from 0.01 to $10^5$ Hz. A bulk electrical conductivity of glasses has been estimated from Argand plots generated from these measurements or by fitting procedure of impedance spectra discussed below. The complex resistance $Z$ measured as a function of angular frequency $\omega = 2\pi f$, can be fitted to a sum of two relaxation functions:

$$Z = \frac{R_1}{1 + (j \cdot \omega \cdot \tau_{e.p.})^p} + \frac{R_2}{1 + (j \cdot \omega \cdot \tau_{d.l.})^n} \quad (16),$$

where the first term in the right hand side of Eq 16 ($R_1$, $\tau_{e.p.}$, and $p$) corresponds to the electrode polarisation process and the second term ($R_2$, $\tau_{d.l.}$ and $n$) stands for the bulk dielectric losses in the sample [44]. The fitting of data to Eq 16 has been done using Argand plots. The Argand diagram is a complex plane locus in which the imaginary part of the complex impedance $Im[Z]$ is plotted against the real part $Re[Z]$ and each point is characteristic of one frequency measurement. Fig. 6 illustrate the Argand plots measure for SiO$_2$ at 0.5 GPa. The intersection of the arc with the $Re(Z)$ axes defines $R_2$, the bulk resistance of the sample. From $R_2$ and the geometric factor $G$ from Eq 15,
the bulk electric conductivity has been calculated, \( \sigma_{d.c.} = 1/(R_2 \times G) \). In the case of SiO\(_2\) and anorthite, we compared the D. C. electric conductivity with results measured at a constant frequency 10\(^3\) Hz. Arrhenius plots of the electrical measurements of the bulk resistance were measured covering a temperature range both below and above the glass transition. The plots indicate a change in slope of the conductivity curve at the glass temperature \( T \sim T_g \). Measurements from the two methods (bulk conductivity measurement from Argand plot and isofrequency measurement) provide the same \( T_g \) for both albite and haplogranite glasses but result in significantly differing \( T_g \) values for both anorthite and silica glasses.

When the fitting of frequency scans of the electric impedance does not permit a reliable estimation of \( R_2 \) from the fitting Eq 16, the D. C. conductivity \( \sigma_{dc} \) has been estimated from Argand-plots as an intersection of \(-Im(Z)\) graph with \( Re(Z)\)-axes [44]. On an Arrhenius type of diagram the \( \sigma_{dc} \) data show two distinct slopes with differing activation energies:

\[
\sigma_{dc} = \sigma_{0,dc} \cdot \exp\left(-\frac{\Delta E_a}{RT}\right) \tag{17}
\]

The kink-point on plots \( \ln(\sigma_{dc}) \) vs \( 1/T \) was used as a characteristic temperature point to discriminate glassy and liquid states only during the first heating cycle(e.g. [30, 31, 45, 46]).

Results

Results of 0.1 MPa experiments

The results of electrical conductivity measurements at 0.1 MPa on albite, haplo-granitic, anorthite and silica glasses are presented in Fig. 7. Electrical conductivities of \( Na \)-bearing glasses (haplogranite, albite) are \( 10^4 \) to \( 10^5 \) times higher than those of anorthite and SiO\(_2\) glasses at comparable temperatures. This difference is attributed to the easy dipole polarisation of sodium bearing glasses. High conductivity in these glasses associated with mobility of \( Na^+ \) ions which diffusivity is higher than other species. Above \( T_g \) the rotation and translation movement of \( Na \)-cations around non-bridging oxygen atoms contribute to the electrical conductivity of \( Na^+ \)-bearing glasses at high frequencies (> \( 10^8 \) Hz). The observed kink of the slope in an Arrhenius plot \( \ln|Z| \) vs. \( 1/T \) (where \( Z \) is the bulk impedance and \( T \) is the absolute temperature) or conductivity \( \ln\sigma_{d.c.} \) vs.
$I/T$, measured at high pressure for $Na$-bearing glasses is significantly lower ($> 50°C$) than $T_g$ estimated from calorimetric and rheological measurements at 0.1 MPa [46, 50]. For anorthite and silica glasses the observed kink in the slope is slightly lower than the calorimetric $T_g$ [51].

As it was mentioned above, for glasses with alkalis, like $Na^+$ in albite and haplo-granitic glass, the activation energy of $\sigma_{dc}$ depends on the mobility of $Na^+$ in the structure. On cooling, at a certain temperature the mobility of a translation motion of alkali ions is not correlated with the thermal structural modifications [35]. In the melt phase, structural elements may always be arranged in an energetically favourable network, leaving minimum space for mobile charged species like $Na^+$. The experiments confirm that $Na$-bearing silicates the activation energy of $\sigma_{dc}$ above the glass transition temperature is higher than below $T_g$. Below the glass transition the mobility of $Na^+$ remains rather high and decoupled from the structural relaxation of SiO$_4$-AlO$_4$ matrix ($\alpha$-relaxation). This is a reason of high frequency relaxation processes in $Na$-bearing silicates which has the features of $\beta$-relaxation. The inflection point on the Arrhenius plot of D. C. conductivity $vs. 1/T$ is shifted toward lower temperatures relative to the structural $T_g$ of SiO$_4$-AlO$_4$ matrix because of the interaction of two relaxation processes, $\alpha$- and $\beta$-relaxation. Thus, for alkali-bearing systems the temperature at which the kink point is observed in electrical conductivity measurements is different from the glass transition temperature estimated from rheological, heat capacity, or dilatometric experiments (see Table 2). The measured activation energies of $\sigma_{dc}$ for albite differs strongly at $T < 683°C$ ($\Delta E_a = 55$ kJ/mol), and at $T > 683°C$ ($\Delta E_a = 90$ kJ/mol). For HPG8 at $T < 774°C$, $\Delta E_a = 90$ kJ/mol, whereas at $T > 774°C$, $\Delta E_a = 120$ kJ/mol. For anorthite at $T < 844°C$, $\Delta E_a = 42$ kJ/mol, and at $T > 744°C$ $\Delta E_a = 80$ kJ/mol. For silica glass at $T < 1050°C$, $\Delta E_a = 100$ kJ/mol, and at $T > 1050°C$ $\Delta E_a = 260$ kJ/mol. In previous estimations of $E_a$ from electrical measurements above and below $T_g$ the reported $\Delta E_a$ values are significantly different: for albite $\Delta E_a$ is $\sim 57$ and $\sim 60$ kJ/mol below and above $T_g$, respectively [45]; for anorthite at 10 kHz $\Delta E_a$ is 118 and 9.3 kJ/mol [46]. For silica glass containing OH-impurities the reported value of $\Delta E_a$ for $\sigma_{dc}$ at $T < T_g$ is $\sim 97$ kJ/mol [48]. Measurements on silica glass films $T << T_g$ at 20-300°C in which alkalis and OH- groups presented at a dilute limit, indicate much smaller activation energy for $\sigma_{dc} \sim 39$ kJ/mol [61] identified as being the hole-like polaron hopping energy.
Structure of Glasses and Electrical Conductivity at 0.1 MPa

The significant difference in electrical conductivity of silica and feldspar glasses might be understood by their differing structures. The structure of feldspar and silica glasses has been determined by X-ray radial distribution analysis [62]. Silica glass has a trydimite-like bonding topology based on stuffed six-membered rings of SiO₄ tetrahedra. Albite glass has the same structure as silica with aluminium substituting for silicon in some of the tetrahedral sites. In order to accommodate sodium cations such a structure has more „void spaces and interstices“ between rings than SiO₂ [62]. In anorthite, the glass structure is based on four-membered rings of SiO₄ and AlO₄ tetrahedra.

The mechanism of electrical conductivity in feldspar and silica glasses may be described as a hopping of alkali-ion (Na⁺ in albite; Na⁺ and K⁺ in HPG8) or Ca²⁺ (in anorthite) from one near Al oxygen site to another. The fraction of non-bridging oxygens in albite and HPG8 structures is about 0. In silica glass, the electrical conductivity mechanism is a hopping process of OH⁻ and alkalis impurities between defect [AlO₄-M]⁰ tetrahedra (AlO₄-alkalie metal centres), as well as interconversion of charged NBO sites by hopping of polarons and electrons [49, 63]. The relative effectiveness of a charge transport mechanism in glasses will depend on average distance and value of energetic barriers between neighbouring NBO-sites or defected SiO₄-tetraedra (hopping activation energy). It will depend also on the concentration of NBO-sites and impurities, and on the relative size of hopping electric charge carriers (Na⁺, K⁺, Ca²⁺ or OH⁻).

The highest electrical conductivity was observed in albite glass. In HPG8 glass Na⁺-ions are partially substituted by larger K⁻-ions, and the concentration of alkali ions is also smaller than in albite (Table 1). The least conductive of the feldspar glasses is anorthite. In anorthite glass the structure is less open compared to albite. Average interatomic distances are 1.63 and 1.66 Å for T-O, and 3.12 and 3.15 Å for T-T for albite and anorthite, respectively [62]. In anorthite Al and Si are the most ordered in comparison with other feldspar glasses, i.e. substitution of Al to Si is less random than in alkali aluminosilicates. Silica glass, Suprasil 300, used in this study possesses the lowest electrical conductivity due to much smaller concentration of defects, OH-groups and [AlO₄-M]⁰ tetrahedra. The lower values of σₑ for SiO₂ and anorthite glasses in comparison with albite and haplo-granitic glasses is due to the greater distances between NBO sites and other Si⁺ and O⁻ defects in the glass structure. Effectively, the longer distance for hopping electrical carriers results in fewer percolation paths for conduction [63].
Experiments in Piston-Cylinder

For high pressure experiments with a piston-cylinder, samples of glasses were ground into powder and pressed into the gap between two coaxial electrodes (see Fig. 3). The bulk electrical conductivity was measured with a temperature step ca. 10°, and plotted on an Argand diagram. The electrical impedance data were collected in a scan with 0.17 log step of frequency from $10^1$ to $10^5$ Hz. Imaginary component of $Z$ for anorthite glass in the glass transition temperature range is shown in Fig. 8, which demonstrates also a low frequency peak due to electrode polarisation. The data of bulk resistance of anorthite presented on an Arrhenius plot demonstrate a significant change of the activation energy of $Z_{dc} = R_2$ of anorthite glass below and above $T_g$ (see Fig.9) allowing the determination of $T_g$ with an accuracy $\pm 5°$. In albite and HPG8 samples there is a noticeable frequency dependence of $Z$ at low frequencies (Fig. 10). Plotted in double log coordinates, the frequency dependence of $Z$ allows estimation of a maximum frequency, $F$, at which the polarisation is observed at each temperature. The temperature dependence (Arrhenius plot) of the occurrence of this frequency $F$ differs above and below $T_g$, providing an alternative way to estimate the glass transition temperature, as shown in Fig. 11. The both methods, Arrhenius plots of bulk resistance and polarisation frequency $F$, provide about the same result of $T_g$. The albite glass possesses a rather high electrical conductivity, and, therefore, may be classified as a “loose” conductor. This class of conducting glasses has also high polarisation (polarisation exponent $n \sim 0.5$) and a broad dispersion range of dielectric properties [35]. The estimation of $T_g$ in albite at 0.5 and 1 GPa are shown in Fig. 12. For albite, similar to the behavior of viscosity vs. pressure, $T_g$ decreases with increasing pressure. The same effect of pressure is observed for the haplogranitic glass. For anorthite and silica glasses $T_g$ is an increasing function of pressure, as may be the viscosity of these melts.

The data of electrical impedance $Im(Z)$ for anorthite glass at 0.3 GPa are shown in Fig. 8. The results of fitting the frequency scan data to Eq 16 are shown in Fig. 8. The temperature dependence of $\tau_{d,l}$ determines the activation energy of the dielectric loss peak c.110 kJ/mol. The parameter $n$ in Eq 16 characterises the broadness of the dielectric loss peak in comparison with a Debye peak ($n=1$). As it follows from Fig. 8 by crossing the glass transition temperature $m$ becomes less than 1 ($n \sim 0.95$). Thus, the anorthite is fragile and “tight” glassy conductor [35]. Silica glass is probably a strong and “tight” glass having low electrical conductivity and polarisation exponent $n$ is close to 1 and slightly decreases with the rising temperature (Fig. 6). In the Argand diagram the bulk
The properties of SiO₂ glass are marked by a perfect semi-circle (Fig. 6). Estimation of \( T_g \) at 0.6 GPa in Suprasil 300 is shown in Fig. 13. The difference in activation energies of \( \sigma_S \) for SiO₂ and albite are very small, 142 and 148 kJ/mol, resulting in a significant error of \( T_g \sim 1080 \pm 20^\circ\text{C} \) (Fig. 13).

### Experiments in Belt-Apparatus and Multi-Anvil Press

The results of electrical conductivity measurements carried out in the belt apparatus are shown in Fig. 14. The change in the slope of the bulk conductivity below and above \( T_g \) is very small for anorthite as a result of increasing pressure and pressure-dependent compressibility of the glass. In albite glass, the difference in the activation energy below and above \( T_g \) is significant. In reality, the kink of the slope in the dependence \( \log(\sigma) \) vs. \( 1/T, K \) for albite glass corresponds to “mobile Na⁺ \( T_g^S \)” because of the presence of “loose” species Na⁺ in the structure [35]. Data [64] for albite glass at \( T < T_g \) and pressures 3-4 GPa are in a good agreement with this study. With the pressure increase, the free volume becomes so small that above and below \( T_g \) the difference of activation energies of hopping process of electrically charged defects or defect-sites becomes negligible in the case of anorthite [64, 65]. In albite glass, the activation energy of the bulk conductivity becomes smaller with the pressure increase. This may be explained by shortening of Na-Na distances in the albite structure, but the distance between Na-site and the nearest oxygen remains the same. According to [34] the Coulomb barrier facing a mobile Na will be lowered by an increase of the electrostatic potential of a pair Na⁺ and his empty site.

Only two experiments were done in the multi-anvil press on anorthite and albite glasses. \( T_g \) in both samples was very hard to detect, but likely corresponds to a maximum decrease of the bulk resistance on the Arrhenius plot (Fig 15). The precision of \( T_g \) determination was about 15°C.

### Discussion of Results

Fig. 16 represents a pressure dependence of the measured \( T_g \) from electrical impedance measurements in four type of experimental facilities: atmospheric furnace, piston-cylinder, belt- and multi-anvil presses. For albite, and HPG8 the pressure dependence of \( T_g \) is negative, for SiO₂ and anorthite is positive. High values of \( T_g \) pressure derivative for HPG8 and SiO₂ are preliminary values estimated pressures below 0.6 GPa. Table 3 summarises the glass transition temperature estimated from electrical conductivity measurements in this study. The absolute value of the
derivative \( dT_g/dP \) decreases with the pressure increase, however, as noted above, \( T_g \) is difficult to estimate at high pressures due to the pressure dependent compressibility. To detect a correct change in glass temperature with pressure at \( P = 0.1 \) MPa perhaps only a short pressure interval is necessary (< 0.1 GPa). Theoretically, the distribution of relaxation times will broaden at high pressure [66] and the transition occurs over a wider temperature range. This would make it impossible to detect \( T_g \) at some critical pressure. In the method which was used in this study, this happens when the activation energies of electrical conductivity below and above \( T_g \) become equal.

Table 4 lists previous estimations of the pressure dependence of \( T_g \). Only one experimental work [67] reports results of in-situ high pressure dilatometric measurements of \( T_g \) on glass samples having very fast cooling rates. \( dT_g/dP \) measured for diopside glass is in a good agreement with calculated glass transition slope from the second Ehrenfest equation [47, 68] and viscosity measurements [6]. The direct measurements of \( dT_g/dP \) on other glass formers indicate that the pressure dependence of \( T_g \) may vary from 200 to 150 K/GPa for \( \text{B}_2\text{O}_3 \) or lead [69] to 3.6 K/GPa for metallic glasses [19].

The viscosity measurements in silicate melts provide an explicit estimations of \( dT_g/dP \). The rheology measurements of albite melt have been studied under pressure up to 7 GPa [2, 3]. It was established that the decrease of albite melt viscosity is about 0.38 log[Pa s]/GPa. Using temperature dependence of viscosity of albite melt, the estimation of the pressure derivative of the glass transition temperature in albite is c. 58 K/GPa.

The glass transition temperature in silica glass is the most poorly characterised because of a high resistivity of \( \text{SiO}_2 \) even at highest temperatures of experiments. \( T_g \) may vary from about 1200°C according to rheology data [70] and calorimetry [52] to 1100-1050°C according to high-temperature light scattering experiments [18, 56] depending on cooling rate, content of OH\(^-\), and annealing temperature. The Prigogin-Defay ratio for \( \text{SiO}_2 \) glass \( \Pi \sim 2 \times 10^5 \) (!) is unexpectedly high, indicating that a single relaxation parameter cannot be used to describe a glassy state [18].

In order to estimate a dielectric relaxation time from measured electrical impedance data \( (Z^*) \) the expressions for the complex modulus as follows were used [44]:

\[
M' - iM'' = \omega \varepsilon_0 \varepsilon G
\]

(18),

where \( G \) is a geometric factor, \( \varepsilon_0 \) is the dielectric constant of a free space, \( \omega \) is angular frequency.
The dielectric relaxation times were calculated from frequency corresponding to a peak of $M''$

$$\tau = (2\pi f_{\text{peak}})^{-1} \quad (19).$$

The direct method to estimate a dielectric relaxation time is to make a fitting of the electrical impedance scans to an equivalent electric circuit, for example Eq 16, and estimate parameter $\tau_{d,l}$. As a result of fitting of the second term in Eq 16, we get $\tau_{d,l}$, the dielectric relaxation time, and $n$, polarisation exponent [65]. Both methods, Eqs 16 and 19 must give the same result, if the impedance data only in the frequency band around dielectric relaxation peak are used. The activation energy of $\sigma_{DC}$ may depend on temperature in the same way as $\tau = \sqrt{RC}$, where $R$ resistivity and $C$ capacity at a peak frequency, only when $R$ and $C$ have the same activation energies and polarisation exponent $n$ is close to 1.

The results of dielectric relaxation measurements for silicate glasses are presented in Fig. 17, and the calculated activation energies of dielectric relaxation are listed in table 4 and compared with the tracer diffusion activation energies. From Fig. 17, the values of dielectric relaxation times of SiO2 and anorthite are smaller than structural or shear stress relaxation for about 4-5 orders of magnitude, and for albite and haplogranite glass this difference is about 7-8 orders of magnitude. This difference in the decoupling index between structural and dielectric relaxation scales supports the idea that SiO2 and anorthite are strongly coupled, albite and haplogranitic glasses are weakly couple glasses [35]. In strongly coupled glasses, SiO2 and anorthite, this difference in activation energies is smaller than in albite, a weakly coupled glass. The difference of activation energy of Na-tracer diffusion and dielectric relaxation in Na2O-3SiO2 has been discussed in [32]. In [32] the calculation of a “tracer diffusion” relaxation time has been done taking into account the spacing of Na-Na between two adjacent structural sites. The dielectric relaxation in weakly coupled glasses has a substantial contribution from Na-hopping on a much shorter distances, around the nearest oxygen site which also results in a charge separation and formation of electric dipoles [33]. In the case of aluminosilicates, like albite and haplogranitic glass, the structural position of Na is near an oxygen belonging to AlO4- complex [34]. In strongly coupled glasses the contribution into electric conductivity due to a charge separation process due to a short distance cation hopping is negligible. This may be reason for the differing contrast between activation energies of tracer diffusion and dielectric relaxation in strongly and weakly coupled glasses below and above $T_g$.

For SiO2 the activation energy of dielectric relaxation below $T_g$ is close to the tracer
diffusion of Si ca. 220 kJ/mol. Above the glass transition $E_a$ of dielectric relaxation is close to $E_a$ of O-trace diffusion or structural relaxation $\sim 515$ kJ/mol [48]. According to the theoretical consideration in [34], the activation energy of the bulk conductivity/tracer diffusion in SiO$_2$ glass has to be equal to the binding energy of an isolated Na to oxygen in this glass $\sim 130$ kJ/mol. In this calculation a distance Na-O is assumed 2.4 Å [36]. As far as Na are at a dilute limit in SiO$_2$, the Coulomb barrier facing Na is not corrected to the attraction energy between a Na-site and a nearest empty Na-site. With the increase of Na-content the activation energy of conductivity/tracer diffusion is equal to the binding energy Na-O corrected (abstracted) to the electrostatic energy of an adjacent Na-Na sites and divided to the Kohlrausch exponent due to the cooperativity effects (or $1-n$, where $n$ is the polarisation index Eq 16). The distance between Na-Na in sodium silicates with a mole fraction of sodium $\sim 0.3$ is c. 3.17 Å [36] and the correction factor for the cooperativity effects $\sim 0.5$. Thus, in a fully polymerised glasses, like albite or haplogranitic glass, the conductivity/tracer diffusion activation energy has to be $\sim 60$ kJ/mol, which was observed in this study at 0.1 MPa.

For anorthite, the reported activation energies are for chemical diffusion $\sim 230-460$ kJ/mol and significantly larger than measured $E_a$ of dielectric relaxation $75-125$ kJ/mol. The compiled data on tracer diffusion in the CaO-Al$_2$O$_3$-SiO$_2$ (40-20-40 wt. %) system indicate that in the glass (600-900°C) $E_a \sim 245$ (for $^{18}$O) and $\sim 255$ (for $^{30}$Si) kJ/mol [76]. In the melt (1550-1350°C) $E_a \sim 230$ (for $^{26}$Al), 290 (for $^{31}$Si) and $\sim 380$ (for $^{18}$O). In the supercooled liquid regime at temperatures just above $T_g$ the activation energy for $^{18}$O tracer diffusion may even be 900 kJ/mol. Smaller activation energies for tracer diffusion of Ca, Al, Si, and O were obtained from molecular dynamic simulations (MD), for anorthite glass ($\sim 110$ kJ/mol), for melt ($\sim 180$ kJ/mol) [77]. The activation energy of dielectric relaxation in albite correlates well with the tracer diffusion of Na and differs from those of Si, Al, and O. From MD simulations, the tracer diffusion coefficients in [78] have activation energies $\sim 80$ kJ/mol for Na, $\sim 280$ kJ/mol for Si, $\sim 290$ kJ/mol for O, and $\sim 270$ kJ/mol for Al. In general, Ca$^{2+}$ and Al$^{3+}$ in silicate melts have rather low mobilities and their presence in the alkaline aluminosilicates may even impede the motion of alkali ions [79].

The estimated $T_g$ in albite glass from electrical impedance measurements characterises only a hopping and charge separation relaxation process of sodium and not related to the structural relaxation. The same is probably true for HPG8. The small scale hopping and charge separation in the electric field is an effective mechanism of the electrical conductivity in sodium aluminosilicates
The hopping of sodium ions between positions adjacent to NBO- (in sodium silicates) and/or Al-tetrahedra (in sodium aluminosilicates) sites may explain the high electrical conductivity of these glasses. The lower values of $T_g$ estimated for albite and HPG8 from electrical impedance measurements in comparison with calorimetric and dilatometric data are indicators of the beginning of a “loose” mobility of Na$^+$ in the structure at temperatures even below rheological or calorimetric $T_g$ (Table 2). The idea of a “decoupling” character of dielectric relaxation from mechanical spectroscopy relaxation in sodium-bearing glasses was discussed in details in [81] on the base of “decoupling” index. Subsequently, the phenomena of alkaline tracer diffusion decoupling from structural relaxation was compiled and presented for geologists in [32, 82]. The activation energies of the dielectric relaxation time and of the diffusion coefficient are summarised in Table 5.

The pressure increase slows down the dielectric relaxation time. This may best be explained by a continuous diminishment of open paths and mobility of alkaline ions, increasing the time for defect diffusion. This correlates with the electrical conductivity measurements in Ag-ionic glasses, where the pressure increase and densification results in a progressive decrease of the electrical conductivity [31, 38]. The temperature dependence of dielectric relaxation in anorthite is plotted in Fig. 18 at three pressures 0.1 MPa, 0.3 and 4.5 GPa. The activation volume of $\tau$ for anorthite glass, calculated as follows,

$$\Delta V^* = \frac{\partial \Delta E_d}{\partial P} \tag{20},$$

is about $+10 \pm 5$ cm$^3$/mol. For albite glass, the pressure dependence of activation energy of conductivity at $T<T_g$ was used (Table 5), and the estimations provide a negative activation volume $-5 \pm 2$ cm$^3$/mol. For comparison, MD simulations [78] of the tracer diffusion in albite provides for Na an activation volume $-3$ cm$^3$/mol, $-4.5$ cm$^3$/mol for Al, $-6$ cm$^3$/mol for Si, and $-5$ cm$^3$/mol for O. From the negative pressure dependence of viscosity the calculated activation volume of the shear viscosity in albite melt at 1900-2000 K and in pressure range 2.6-5.3 GPa is $-5.4$ cm$^3$ mol$^{-1}$ [2]. It should be noted here that the experimental error of the data in Fig. 18 is rather large, the data were collected in three different apparatus (atmospheric pressure furnace, piston-cylinder and belt apparatus), having differing sample geometries and temperature fields.

Table 6 summarises the literature data on parameters used in calculations of Prigogin-Defay parameter and the pressure dependence of $T_g$ for studied silicate glasses. The span of parameter $\Pi$ is one order of magnitude and, in average, it is much higher than 1 for all silicate glasses. The
extreme high value of \( \Pi = 1.7 \times 10^4 \) is calculated for SiO\(_2\) by using the thermal expansion coefficient measurements from [53]. However, if one uses the thermal expansivity data from [90] the value of \( \Pi \) for silica glass may be even close to 1. In the present work, the upper limit of \( \Pi \) estimated for SiO\(_2\) glass by assuming that \( \Delta \alpha \sim \alpha \) from [53]. In reality, the thermal expansion coefficient of silica glass is negative at temperatures up to 100-150° above \( T_g \) and, then, above 2000K becomes again positive \( \sim 10^{-4} \) K\(^{-1}\)[53]. In [17] the \( \alpha \) of SiO\(_2\) was erroneously averaged in the wide temperature interval and the suggested \( \Delta \alpha \) between silica glass and melt \( \sim 1.1 \times 10^{-5} \) K\(^{-1}\) is too small. For the calculation of \( \Pi \) for albite (from 15 to 3) and anorthite (from 38 to 7), the authors [17] used rather arbitrary values of \( \Delta \beta \) (the contrast of isothermal compressibilities in glass and in melt has been taken from 1 to \( 5 \times 10^{11} \) Pa\(^{-1}\)). In the present estimation of \( \Pi \), the experimental compressibility of melt was calculated by using the method of [95] and extrapolated data of [93]. The contrast in compressibility between melt and glass was assumed to be \( 0.5 \beta_T \) of the melt. In reality, \( \Delta \beta_T \) may cover a much broader span. For example, in metallic glasses \( \Delta \beta_T \) is about 1% of \( \beta_T \) [19], in SiO\(_2\) \( \Delta \beta \) is about 75% of \( \beta \) [18, 96]. For albite glass, the compressibility from the measurements of glass density at high pressure were also used [94]. A comparison between calculated and measured \( dT_g/dP \) in electrical impedance experiments indicates that only SiO\(_2\) and anorthite (if only data at pressures \(< 1 \) GPa are taken into account) are in a satisfactory agreement (Table 6). Otherwise, \( T_g \) and \( dT_g/dP \) estimated from electrical impedance data for alkaline aluminosilicates are very different from the structural glass transition. But even for anorthite, for which the present estimations of \( T_g \) are close to the structural glass transition, the \( \Pi \) value is much larger than 1, which does not permit consideration of the glass transition in anorthite as a second order phase transition, i.e. a relaxation process with one ordering parameter.

The results of \( T_g \) estimation from electrical impedance measurements provide different results in comparison with rheological, calorimetric or dilatometric measurements. There are few reasons for that. The question which arises, is it right to compare dynamic methods of \( T_g \) determination using variable frequency and methods using down- and up-scan definitions of \( T_g \) [1]. Usually, dynamic or A.C. methods result in higher values of \( T_g \) in comparison of time scanning of heating-cooling cycles. The observation in the present study of the small difference of \( T_g \) for anorthite and SiO\(_2\) may be attributed to the difference in the definition of \( T_g \): as the midpoint of the specific heat capacity rise in a heating temperature scan and as a temperature of the maximum in imaginary part of the electrical impedance. For alkaline bearing glasses the observed difference in
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$T_g$ obtained from electrical measurements, from one hand, and rheological, calorimetric or dilatometric studies, from other hand, is more fundamental. Essentially, the difference in the relaxation time of mechanical and electric properties lies in the differing nature of contributions of these two relaxation and may attain a factor of $10^{1.2}$ near $T_g$ for some glass formers [30, 35]. There is a contribution from two processes to electric relaxation, charge separation and charge migration. Thus, it may expected that in glass where charge separation is significant, will behave differently from glasses where charge transport is mostly due to a charge carrier migration. In silicate glasses and melt containing in the structure $Na^+$ the effects of charge separation are very important, sodium is highly unharmonic species, especially, in the aluminosilicate structure. Sodium ions are responsible for a significant polarisation ($n$~0.5 in Eq. 16). By replacing $Sr^{4+}$ to $Al^{3+}$ sodium becomes surrounded by several non-bridging oxygen ions and aluminium tetrahedra which results in an increase of the dielectric constant and increase of ionic polarisability with the increase of aluminium substitution [80]. The albite and haplo-granitic glasses due to their high conductivity and polarisability can be classified as “loose” glass formers. The $T_g$ measured in these glasses by electrical impedance method is a temperature above which $Na^+$ ions become sufficiently mobile in comparison with the rest of the structure, and the kink in the slope $ln(\sigma)$ vs. $1/T.K$ corresponds to “mobile $Na$-ion $T_g$‘s“ [81]. In other word, this break in the temperature of the secondary ($Na$-ion mobility relaxation) at $T_g^{Na}$ is due to a persisting long range sodium mobility while the long range motion of atoms constituting the rest of the structure (O, Si, Al) is almost frozen below $T_g^{Na}$.

The differing behaviour of the activation energy of the dielectric relaxation in anorthite and $SiO_2$, from one hand, and albite and haplogranitic glass, from other hand, relates to the structures of these glasses. With the pressure increase, all interatomic distances in anorthite and $SiO_2$ becomes smaller due to the densification of their structure. Thus, the distance between a alkaline cation and an oxygen sites decreases which results in an increase of the electrostatic binding energy and, therefore, the activation energy of electric conductivity. In alkaline bearing glasses like haplogranitic and albite glasses where alkali concentration is not at a dilute limit, sodium sites are mostly concentrated in channels and clusters due to a microsegregation of their structures [34]. Therefore, the pressure increase influences the distances between alkaline site in a larger extent than alkali – oxygen distances. As a result of this, under pressure the correction of the Coulomb binding energy will be lowered by an increasing electrostatic energy between alkali sites and the macroscopic activation energy of the electric conductivity decreases with pressure for these glasses.
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Judging from the sign of \( dT_g/dP \) for studied glasses and qualitative behavior of the fragility index \( m \) from Eq 10-12, it may be concluded that “loose” conductive glasses (albite and haplogranite) becomes even more fragile with the pressure increase, and “tight” glasses (anorthite and \( \text{SiO}_2 \)) are getting more stronger under pressure. In other word, with the pressure increase and “free volume” decrease the charge carrier motions becomes increasingly oscillatory in alkaline-bearing glasses. This provide a further separation of slow diffusive from fast oscillatory modes [35]. In the case of albite or haplogranitic glass under pressure, the “caging” effect of oxygen atom displacements may result in a highly decoupled diffusion motion for the “loose” sodium atoms and in a reduce of “Na glass transition temperature” \( T_g^{\text{Na}} \). This associates with a decrease of the energetic barries of sodium self-diffusion and electric conductivity. In the case of anorthite and \( \text{SiO}_2 \) or insulating glasses, the “caging” effect extends to all structural species reducing the gap between fast and slow modes. The energetic barriers for the diffusion motions of atoms and the activation energy of electrical conductivity at \( T_g \) in these glasses increase under pressure.

Conclusions

1. The use of electrical impedance measurements to determine a glass transition temperature at high pressures provides results for anorthite and silica glasses consistent with previous studies. According to the structure of these glasses, the transport or diffusion of structural and electrically charged defects are correlated. Anorthite may be classified as a “tight” fragile glass former, silica glass is a “tight” strong glass. For albite and haplogranitic glasses the established \( T_g \) is not a structural glass transition because of the “decoupling” between alkaline mobility/charge separation and structural relaxation, the estimated glass transition temperature is \( T_g^{\text{Na}} \). These glasses belong to a class of “loose” glassy conductors.

2. Pressure dependence of \( T_g \) estimated from electrical conductivity measurements reflects viscosity variations with pressure. For albite, the negative slope \( dT_g/dP \) corresponds to a decrease of the shear viscosity of albite melt under pressure. The greatest variation of \( T_g \) with pressure occurs at \( P < 1 \) GPa. Further decrease of \( T_g \) is hindered by a decrease of percolation paths for conduction. As a result of this, the contrast between electrical conductivity below and above \( T_g \) becomes indistinguishable at pressures above 1 GPa.

3. Effect of pressure on dielectric relaxation times and the activation energy of dielectric relaxation may be explained in terms of the activation volume. Positive activation volume
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relates to a positive \( dT_g/dP \) and a “tight” conductance behavior under pressure (SiO\(_2\), anorthite). Negative volume correlates with the negative \( dT_g/dP \) (alkalis-bearing aluminosilicates at non-dilute limit of alkalis) and with a “loose” electric conductance. This differing behavior of
dielectric relaxation under pressure correlates with the classification of glasses into two groups:
glasses with strongly and weakly coupled viscous and dielectric relaxations.

4. The determined \( dT_g/dP \) values compared with those calculated from the second Ehrenfest
relationship show a large discrepancy. Combined with the fact that a significant deviation of the
Prigogin-Defay ratio from 1 is observed, this indicates a difference of the glass transition in silicates from a model of the second order phase transition.

Acknowledgements

The experimental works has been supported by Deutsche Forschungsgemeinschaft in the frame of Special Program „Melts in the Earth: structure, formation and properties“ (SPP 1015). The authors grateful to H. Höfer and T. Stachel for the help with the microprobing. Multi-anvil experiments were performed at Bayerisches Geoinstitut under the EU “TMR – Large Scale Facilities“ programme (Contract No. ERBFMGECT980111 to Prof. D. C. Rubie). A. S. and V. B. thank Exchange Visitor Program between DFG and Russian Academy of Sciences for covering their travel and stay costs at Univ. Frankfurt.

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### Tables

#### Table 1. Composition of glass samples (in wt. %)

<table>
<thead>
<tr>
<th>Oxide</th>
<th>CaAl$_2$Si$_2$O$_8$ Starting composition</th>
<th>CaAl$_2$Si$_2$O$_8$ After experiment</th>
<th>NaAlSi$_3$O$_8$ Starting composition</th>
<th>NaAlSi$_3$O$_8$ After experiment</th>
<th>HPG8</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>42.63</td>
<td>42.62</td>
<td>67.76</td>
<td>67.53</td>
<td>77.9</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>36.86</td>
<td>37.14</td>
<td>19.58</td>
<td>21.37</td>
<td>11.89</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>12.09</td>
<td></td>
<td>10.39</td>
<td></td>
<td>4.53</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0.21</td>
<td></td>
<td>0.27</td>
<td></td>
<td>4.17</td>
</tr>
<tr>
<td>CaO</td>
<td>20.13</td>
<td>19.89</td>
<td>0.18</td>
<td>0.21</td>
<td></td>
</tr>
<tr>
<td>Sum:</td>
<td>99.62</td>
<td>99.65</td>
<td>99.82</td>
<td>99.77</td>
<td>98.48</td>
</tr>
<tr>
<td>Cooling rate, K/h</td>
<td>20</td>
<td>20</td>
<td></td>
<td></td>
<td>300</td>
</tr>
</tbody>
</table>

Microprobe analysis JEOL JXA – 8900RL, 20 kV, sample current 20nA, average of 3-5 points
Table 2. Glass transition temperature $T_g$ (°C) at 0.1MPa

<table>
<thead>
<tr>
<th>Glass</th>
<th>Cooling rate, K/h</th>
<th>Viscosity</th>
<th>Calorimetry &amp; DTA</th>
<th>Volume expansion</th>
<th>Electrical conductivity</th>
<th>Light scattering</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>slow (?)</td>
<td>1150±20 [54]</td>
<td>1180±70 [52]</td>
<td>1100±20 [53]</td>
<td>1050±10 [t. s.]</td>
<td>1100±20 [18]</td>
</tr>
<tr>
<td></td>
<td>slow (?)</td>
<td></td>
<td>1190±25 [55]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaAl$_2$Si$_2$O$_6$</td>
<td>5</td>
<td>839 [38]</td>
<td>865±3 [59]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>8</td>
<td></td>
<td>840±3 [57]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>20</td>
<td></td>
<td>845±3 [57]</td>
<td></td>
<td></td>
<td>820±5 [46], 844±4 [t. s.]</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td></td>
<td>878±5 [59]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>837 [50]</td>
<td>875±5 [59]</td>
<td></td>
<td></td>
<td>813±9 [58]</td>
</tr>
<tr>
<td></td>
<td>132</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>600</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>836 [51]</td>
</tr>
<tr>
<td>NaAlSi$_3$O$_8$</td>
<td>5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>20</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>678±3 [46], 683±5 [t. s.]</td>
</tr>
<tr>
<td></td>
<td>slow (?)</td>
<td>765 [38]</td>
<td>763±11 [58]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>761 [50]</td>
<td>737±5 [59]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>40</td>
<td></td>
<td>734±5 [59]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>132</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>763±11 [58]</td>
</tr>
<tr>
<td></td>
<td>fast (?)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>800±10 [60]</td>
</tr>
<tr>
<td>HPG8</td>
<td>300</td>
<td>864±5[H39]</td>
<td>856 [40]</td>
<td>856±3 [40]</td>
<td>774±5 [t. s.]</td>
<td></td>
</tr>
</tbody>
</table>

[t. s.] – this study, in [54] $T_g$ has been reported as corresponding to $10^{13.2}$ Pa s, in [60] $T_g$ is for quenched sample.
Table 3. Results of $T_g$ (°C) from electrical conductivity data (this study)

<table>
<thead>
<tr>
<th>Pressure, GPa</th>
<th>Albite</th>
<th>Anorthite</th>
<th>HPG8</th>
<th>Suprasil 300</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 MPa</td>
<td>683±4</td>
<td>844±5</td>
<td>774±5</td>
<td>1050±10</td>
</tr>
<tr>
<td>0.3 GPa</td>
<td>847±6</td>
<td>769±6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>690±3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.6 (0.7*)</td>
<td>863±6*</td>
<td>747±6</td>
<td>1080±20</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>676±5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>663±5</td>
<td>859±6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.5</td>
<td></td>
<td>873±6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>630±15</td>
<td>881±15</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*measured at 0.7 GPa

Table 4. Pressure Dependence of Glass Transition Temperature of Some Silicate Glasses $dT_g/dP$ (K/GPa)

<table>
<thead>
<tr>
<th></th>
<th>Cooling rate</th>
<th>Diopside</th>
<th>Albite</th>
<th>Anorthite</th>
</tr>
</thead>
<tbody>
<tr>
<td>¹[67]</td>
<td>22-28 °C/min</td>
<td>+37±3</td>
<td>-25±10</td>
<td></td>
</tr>
<tr>
<td>²[6]</td>
<td>calculated from viscosity</td>
<td>+34±14</td>
<td>-70±8</td>
<td>-4±17</td>
</tr>
<tr>
<td>³[68]</td>
<td>+49±3</td>
<td>+108±40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calculated from Eq 5 using $\Delta V^*$ and $E_a$</td>
<td>20°/h</td>
<td>-120±50</td>
<td>150±50</td>
<td></td>
</tr>
<tr>
<td>From electrical conductivity in this study</td>
<td>20°/h</td>
<td>-9.4±2</td>
<td>+5.3±1.5</td>
<td></td>
</tr>
</tbody>
</table>

¹DTA measurements at pressures up to 0.7 GPa, ²indirect estimations using WLF-equation at 0.1 MPa and the viscosity data at pressures up to 1.5 GPa (no cooling rate are reported), ³calculated from thermodynamic data and Eq 6, no cooling rate reported. In the original paper this result is swapped with the result of [67].
Table 5. Activation energy of the diffusion coefficient and the dielectric relaxation time (in kJ/mol)

<table>
<thead>
<tr>
<th>Ions</th>
<th>SiO₂</th>
<th>CalAl₂Si₂O₈</th>
<th>NaAlSi₂O₈</th>
<th>KAlSi₃O₈ and HPG₈</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH⁻</td>
<td>83 (1100-500°C)¹</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>237 (1200-800)²</td>
<td>230 (845-765)⁶</td>
<td>337 (1500-1100°C)⁸</td>
<td></td>
</tr>
<tr>
<td></td>
<td>579 (1410-1113)³</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>48 (250°C)⁴</td>
<td>247 (760-760)⁶</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>516 (2500-1250°C)⁵</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>327(1600-1350)⁷</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>462 (1600-1350)⁷</td>
<td>425 (1500-1100°C)⁸</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>56 (800-350)⁹</td>
<td></td>
<td>79 (800-350)⁹</td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>99.5 (1000-350)⁹</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| $E_a$¹⁰ in    | 222 (0.1 MPa, T<Tₕ) | 74 (0.1 MPa) | 55 (0.1 MPa, T<Tₕ) | 98 (0.1 MPa, HPG8) |
| this         | 515 (0.1 MPa, T>Tₕ) | 111 (0.3 GPa) | 99 (0.1 MPa, T>Tₕ) | 84 (0.3 GPa, HPG8) |
| study.       | c. 150 (0.6 GPa) | 118 (4.5 GPa) | 48 (0.5 GPa T<Tₕ) | 40 (0.1MPa)¹¹ |
|              |                   |             | 29 (1 GPa T<Tₕ) |                   |
|              |                   |             | 16 (3 GPa T<Tₕ) |                   |
|              |                   |             | 64 (0.1 MPa)¹¹ |                   |

¹ effective OH diffusion [83], ² effective SiOSi diffusion [83], ³ tracer diffusion of $^{28}$Si [84], ⁴ $^{18}$O diffusion in silica glass [85], ⁵ estimated from viscosity measurements and Eyering equation [86], ⁶ tracer diffusion of $^{18}$O and $^{28}$Si in CaAlSiO₄ [84], ⁷ chemical diffusion of CaO/MgO and Al₂O₃ between diopside-anorthite compositions [87], ⁸ self-diffusion of Si and tracer diffusion Al /Ga [88], ⁹ tracer diffusion of $^{23}$Na and $^{40}$K [89], ¹⁰ $E_a$ is the activation energy of dielectric relaxation (D.R.) measured in this study, ¹¹ activation energy of dielectric relaxation calculated from electrical impedance data [46].
### Table 6. Prigogine-Defay ratio and pressure dependence of glass transition temperature.

<table>
<thead>
<tr>
<th>Δα·10⁻⁵ K⁻¹</th>
<th>Anorthite</th>
<th>SiO₂</th>
<th>Albite</th>
<th>HPG8</th>
<th>Orthoclase</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.3 [58]</td>
<td>0.135 [53]</td>
<td>0.76 [58]</td>
<td>1.7 [40]</td>
<td>0.8 [58]</td>
<td></td>
</tr>
<tr>
<td>1.9 [50]</td>
<td>10.3 [90]</td>
<td>3.3 [91]</td>
<td></td>
<td></td>
<td>2.4 [92]</td>
</tr>
<tr>
<td>3.0 [91]</td>
<td>1.1 [17]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Δβ·10⁻¹¹ Pa⁻¹</td>
<td>2.5-2 [93]</td>
<td>5.7 [18]</td>
<td>4.3 [94]</td>
<td>3.7³ [93]</td>
<td>4.5-4³ [93]</td>
</tr>
<tr>
<td>1.9²[95]</td>
<td>6.3 [96]</td>
<td>2.1² [95]</td>
<td>2.1² [95]</td>
<td>2.5² [95]</td>
<td></td>
</tr>
<tr>
<td>56.3 [92]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>37 [92]</td>
</tr>
<tr>
<td>V·10⁻⁶ m³ mol⁻¹</td>
<td>110 [58]</td>
<td>27.4 [18]</td>
<td>112 [58]</td>
<td>28.2 [36]</td>
<td>112¹ [97]</td>
</tr>
<tr>
<td>Π</td>
<td>22-1.5</td>
<td>7.6·10³ - 1.2</td>
<td>135 – 4.2</td>
<td>34-18</td>
<td>200 – 20</td>
</tr>
<tr>
<td>dT_g/dP, K GPa⁻¹</td>
<td>185 - 47</td>
<td>470 – 6</td>
<td>150 - 33</td>
<td>70-64</td>
<td>145 – 28</td>
</tr>
</tbody>
</table>

| K GPa⁻¹ | 5.3 | 50 | -9.4 | -45 |
| dT_g/dP, K GPa⁻¹ | 30 (P< 1GPa) |

¹ calculated from [97]; ² Δβ is a half of the calculated isothermal compressibility 0.5 β_f from [95]; ³ data are extrapolated from [93]; [ts] – from electrical conductivity measurements, this study.
Figures:

**Fig. 1.** Angell plot of samples used in the electrical conductivity study [38]. The fragility index varies from 17 for SiO₂ to 42 for anorthite. Viscosity data for haplogranitic glass HPG8 are from [7, 39].
Fig. 2. Scheme of the electrical conductivity experiments at 0.1 MPa: 1 – Pt-wire furnace ROR Heraeus™, 2 – Al₂O₃ ceramic rods AL23 Frialit-Degussit™, 3 – insulating casting body; 4 – inlet for inert gas (Ar), 5 – flat spring, 6 – electrode contact of Pt-wire, 7 – thermocouple S-type Pt-PtRh, 8 – sample of glass, 9 – sputtered area of sample, 10 – teflon guiding plug, 11 – Pt-foil cemented to the surface of Al₂O₃ rods, 12 – inner Al₂O₃ tube, 13 – elongation gauge.
Fig. 3. Principal scheme of a piston-cylinder cell used for electrical impedance measurements [41]: 1 - inner cylindrical Pt-electrode; 2 - outer cylindrical Pt-electrode; 3 - sample; 4 - thermocouple S-type; 5 - Al₂O₃ – ceramic; 6 - graphite heater; 7 - CaF₂ pressure transmitting medium; 8 - boronitride; 9 – boron nitride ceramic; 10 - hard metal core; 11 - hard metal piston; 12 - plug of stainless steel; 13 - unfired pyrophyllite; 14 - copper-ring; 15 - ground.
Fig. 4. Principal scheme of the electrical impedance measurement in belt apparatus (height 16 mm [42]). 1 – sample (diameter 2.1 mm, thickness 1 mm); 2 – electrical shield from Pt-foil; 3 – electrodes from Pt-foil; 4 – Al₂O₃ ceramics; 5 - thermocouple; 6 – pyrophyllite; 7 - graphite heater; 8 – boron nitride.
Fig. 5. A. Principal scheme of electrical conductivity measurements in multi-anvil press [43]: 1 – MgO, 2 – ZrO$_2$, 3 – LaCrO$_3$ furnace, 4 – MgO, 5 – Mo shield, 6 – Al$_2$O$_3$, 7 – Electrode wire, 8 – Pt – electrode, 9 – sample, 10 – Thermocouple wire (electrode), 11 – Mo, 12 – Al$_2$O$_3$ cement, 13 – pyrophyllite. B. The cross-section of the cell with anorthite glass sample after experiment. Thickness of the sample is 1 mm, diameter 2.1 mm.
Fig. 6. Argand diagram of Suprasil 300 silica glass at 0.5 GPa. The bulk resistance $R_z$ is estimated from fitting of the impedance scans to Eq 16. $R_z$ is also corresponds to the intersection $Im(Z)$-plot with the $Re(Z)$-axes. The impedance arc represents a perfect semicircle. With temperature increase the deviation from Debye relaxation, , is slightly increases, i.e. parameter $n$ decreases. Thus, silica glass belongs to a class of “tight” and strong glassy conductors [35].
Fig. 7. Results of the bulk electrical resistance $\sigma_b$ measurements at 0.1 MPa. The kink in the slope of the Arrhenius dependence of the bulk electrical conductivity indicates the glass transition temperature for mobile cations in the structure of Ab, HPG and An glasses. In SiO$_2$ glass the charge carriers are impurities, like OH-species and alkalis at a dilute limit.
Fig. 8. The imaginary component of electrical impedance of anorthite at 0.3 GPa. The frequency scans of the electric impedance have been fitted to Eq 16 for each temperature. With the temperature increase the dielectric relaxation peak shifts toward high frequencies as indicated by the arrow. The deviation from Debya peak increases via decreasing parameter n (numbers in brackets). At $T>T_g$ $n$ becomes less than 1. Anorthite glass is a fragile and “tight” glassy conductor [36].
Fig. 9. Results of electrical resistance measurements in anorthite glass at 0.3 (upper panel) and 0.7 GPa (lower panel). The measurements of D.C. resistance at a fixed frequency are compared with bulk resistance obtained from Argand plots and fitting parameter R2 in Eq 16. Bulk D. C. resistance measurements provide higher values of \( T_g \) (solid arrows) in comparison with measurements at fixed frequency according to [35].
Fig. 10. Method of estimation of the polarisation frequency \( F \). The intersection point of two derivatives \( \frac{\text{d} \log(Z)}{\text{d} \log(f)} \) calculated at \( f > 1 \text{ Hz} \) and \( f < 1 \text{ Hz} \), corresponds to polarisation frequency \( F \) which was used for determination of "mobile Na-ion \( T_g \)" (left panel). At 0.6 GPa the data of polarisation frequency \( F \) (Hz) are plotted as a function of \( 1/T \), K. Right panel is a polarisation frequency \( F \), determined from frequency scans at different temperatures. The kink in the slope on the \( F \)-graph corresponds to the kink in the slope on the electrical impedance curve Fig 11.

Fig. 11. Estimations of glass transition temperature from electric impedance measurements in HPG8 glass at 0.3 and 0.6 GPa at fixed frequency \( 10^3 \text{ Hz} \) and D. C. resistivity.
Fig. 12. Glass transition temperature in albite glass under pressure 0.5 (upper panel) and 1 GPa (lower panel). Arrows indicate $T_g$, the temperature point at which the activation energy starts to increase with the rising temperature.
Fig. 13. Estimation of the glass transition temperature in SiO₂ Suprasil 300 at 0.6 GPa from the change in the activation energy of the D.C. resistance calculated from impedance frequency scans and Eq 16. The Argand plots are shown in Fig. 6.
Fig. 14. Results of electrical conductivity and $T_g$ measurements in the belt apparatus on albite (upper panel) and anorthite (lower panel) glass samples.
Fig. 15. Estimation of $T_g$ at 6 GPa in multi-anvil press in albite (upper panel) and anorthite (lower panel). For albite the Argand plot was not possible to construct because of a low frequency noise, thus, only measurements at constant frequency ($10^3$ and $10^2$ Hz) were used to identify $T_g$ in the Arrhenius plot.
Fig. 16. Pressure dependence of the glass transition temperature from electrical impedance measurements. The slope of the pressure dependence of $T_g$ at low pressures is higher than in the whole pressure range.

$$T_g = 50^\circ /\text{GPa} \times P(\text{GPa}) + 1050^\circ \text{C}$$

$$T_g = 5.3^\circ /\text{GPa} \times P(\text{GPa}) + 848^\circ \text{C}$$

$$T_g = -45^\circ /\text{GPa} \times P(\text{GPa}) + 777^\circ \text{C}$$

$$T_g = -9.4^\circ /\text{GPa} \times P(\text{GPa}) + 688^\circ \text{C}$$
Fig. 17. Temperature dependencies of dielectric vs. structural relaxation time for silicate glasses. Dielectric relaxation time has been estimated from impedance measurements by using Eqs 16 and 19. For HPG8 at 0.6 GPa the dielectric relaxation time is taken as $1/F$, a reciprocal polarisation frequency. The structural relaxation time has been calculated from shear viscosity data at 0.1 MPa by using the Maxwell relationship $\tau(s) = \eta (Pa \ s)/25$ GPa. For SiO$_2$ (solid bold line) the data are from [48]; for anorthite (solid thin line) the shear viscosity data are from [58, 71, 72]; for albite (dashed line): 1 – shear viscosity from [71, 73], 2 – from [47, 68, 74]; for HPG8 (dotted line) the shear viscosity from [7, 39, 75].
Fig. 18. Dielectric relaxation time of anorthite glass as a function of pressure. $\Delta V^*$ is the activation volume calculated at 800°C according to Eq 20.