Electrical conductance of molten silicates
Application of the free volume theory

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Electrical conductance in $CaO—MgO—SiO_2$ melts has been interpreted using the free volume theory proposed by Cohen and Turnbull for mass transport in liquids. The temperature dependence of the conductivity activation energy has been determined. Calculated activation energy values were used to test an exponential relation between conductivity and temperature

$$x = A'(c - c^0)\ T^{-1/2} \exp\left[-k/(T - T_0)\right]$$

derived on the basis of the free volume theory. Calculated values T_0, which according to the applied theory should approach transformation temperature decrease with increasing concentration of conductive particles, *i.e.* with successive destruction of anionic network.

It was established that the charge transport in the investigated system is satisfactorily described by the free volume theory, and the temperature T_0 as well as the concentration of conductive particles are determining factors of the conductivity.

Теория свободного объема, разработанная Коэном и Тернбуллом для переноса материи в жидкостях была использована для объяснения электропроводности в расплавах системы $CaO—MgO—SiO_2$. Была установлена зависимость активационной энергии электропроводности от температуры. Рассчитанные значения энергии активации были использованы при проверке экспоненциальной формулы для зависимости электропроводности от температуры

$$x = A'(c - c^0)\ T^{-1/2} \exp\left[-k/(T - T_0)\right]$$

выведенной на основе теории свободного объема в расплавах. Рассчитанные величины T_0, которые в соответствии с использованной теорией должны быть близки температуре трансформации понижаются при увеличении концентрации проводящих частиц, то есть со степенью разрушения анионной сети. Обнаружено, что теория свободного объема хорошо

описывает перенос заряда в изучаемой системе, причем температура T_0 и концентрация проводящих частиц являются факторами, определяющими величину электропроводности.

The validity of the free volume theory proposed for mass transport in liquid systems by *Cohen* and *Turnbull* [1] was verified in a number of liquid systems including molecular liquids and molten metals [1], molten nitrates and chlorides [2] and fluorides [3]. This theory was applied in a not fully rigorous manner for the case of electrical conductance of polycomponent oxide glasses [4]. Taking into account the glass-forming character of the latter melts, a satisfactory description of transport properties by the free volume theory can be anticipated also in this case.

According to original concept of the transport process, based on the free volume theory [1] a particle of a liquid may undergo a translation displacement only when a void above a certain critical size v^+ sufficiently large for the placement of a particle appears adjacent to it. Such voids may arise without energy change by redistribution of "free" volume in the liquid, which is taken as equal to the increase of volume of the liquid due to heating above temperature T_0, where free volume begins to appear. The temperature T_0 lies very close to experimentally determined transformation temperature T_g and is identical with T_g for infinite relaxation time. Translation movement of a particle is then given by the probability of occurrence of such a void and this was shown to be an exponential function of the ratio of the critical void volume v^+ to the total free volume v_f [1]. For individual transport properties w_i the following expression can be derived

$$w_i = A_i \exp\left(-\gamma v^+ / v_f\right) \tag{1}$$

where w_i for diffusion is $D \cdot T^{-1/2}$, for fluidity $\Phi \cdot T^{1/2}$, and for conductivity $\varkappa \cdot T^{1/2}$, γ is the factor to correct for overlap of free volume acquiring a value from the range 0.5—1 and A_i is a constant with different values for individual transport property independent of both temperature and composition. In eqn (1) the free volume can be expressed as

$$v_f = v - v_0 \doteq \alpha \bar{v}(T - T_0) \tag{2}$$

where v is the actual volume of liquid, v_0 is the volume of close-packed random arrangement of particles of the liquid, α is the mean expansion coefficient, and $\bar{v}$ is the mean volume in the range $T - T_0$. Then for the temperature dependence of a transport property we obtain

$$w_i = A_i \exp\left[-k/(T - T_0)\right] \tag{3}$$

where $k = \gamma v^+ / \alpha \bar{v}$. This equation is analogical with well-known Vogel—Fulcher—Tamman's equation in which the member $T^{\pm 1/2}$ is often omitted and which is used routinely for the description of the viscosity in glass-forming oxide melts.

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Theoretical

In a previous paper [5] the conductivity of $CaSiO_3$—$CaMgSi_2O_6$—$Ca_2MgSi_2O_7$ melts in the range 1670—1920 K was determined. The dependence of the conductivity $\varkappa$ on the composition was described by the equation

$$\varkappa = \sum_i z_i F u_i (c_i - c_i^0) \tag{4}$$

where c_i is the concentration (mol cm^{-3}) of conductive particles with number of elementar charges z_i and mobility u_i (cm^2 s^{-1} V^{-1}), F is Faraday's constant, and c_i^0 is the limiting concentration of conductive particles at which the conductivity in the CaO—SiO_2 and MgO—SiO_2 systems decreases to zero. When diffusion coefficients D_i from Nernst—Einstein's equation are substituted for mobility u_i in eqn (4) we obtain

$$\varkappa = \sum_i z_i F^2 D_i (c_i - c_i^0)/RT \tag{5}$$

In the given case the equation can be rearranged by summation for cations Ca^{2+} and Mg^{2+}. As the diffusion coefficients of both cations of the investigated system have similar values [5], their mean value calculated *e.g.* according to the relation $\bar{D} \doteq 2D_1 D_2/(D_1 + D_2)$ [6] can be substituted for D_i. When the sum $c = c_{Ca^{2+}} + c_{Mg^{2+}}$, *i.e.* the total concentration of all conductive particles is substituted for c_i we get

$$\varkappa = \frac{2F^2}{RT} \bar{D}(c - c^0) \tag{6}$$

The temperature dependence of $\bar{D}$ given by eqns (1) and (3) is substituted for $\bar{D}$ in eqn (6) and we obtain

$$\varkappa = \frac{2F^2 A}{R} (c - c^0)\, T^{-1/2} \exp\left[-k/(T - T_0)\right] \tag{7}$$

Eqn (7) describes conductivity in the system CaO—MgO—SiO_2 in terms of temperature and composition. Taking natural logarithms and deriving with respect to $1/T$ yields

$$\frac{d \ln \varkappa}{d(1/T)} = \frac{d \ln (c - c^0)}{d(1/T)} + T/2 - k\left(\frac{T}{T - T_0}\right)^2 \tag{8}$$

The expression on the left side of eqn (8) defines the activation energy of the conductivity $E_\varkappa = -R\left[\dfrac{d \ln \varkappa}{d(1/T)}\right]$. Letting

$$c - c^0 = \Delta c = \frac{\Delta n}{\Delta V} \tag{9}$$

gives

$$\frac{d \ln \Delta c}{d(1/T)} = -\frac{d \ln \Delta V}{d(1/T)} = \Delta\alpha \ T^2 = (\alpha - \alpha^0) \ T^2 \doteq \alpha T^2 \qquad (10)$$

where n is the amount of conductive particles, V is the molar volume of given melt, α and α^0 are the coefficients of volume expansion of given melt and of the melt with limiting concentration c^0, respectively. α^0 can be neglected because at concentration c^0 the composition of melt is close to SiO_2 which has according to [7] α approaching zero. After these rearrangements eqn (8) acquires the form

$$E_{corr} = E_x + \alpha \ RT^2 + RT/2 = kR\left(\frac{T}{T - T_0}\right)^2 \qquad (11)$$

This equation is identical with that derived by *Angell* [2] for testing the validity of the free volume theory. A corrected activation energy of the conductivity E_{corr} should be sole linear function of $[T/(T - T_0)]^2$ for all investigated melts and has to pass through the origin. The calculation was made for melts of the system $CaSiO_3$—$CaMgSi_2O_6$—$Ca_2MgSi_2O_7$ using conductivities determined in [5]. The values of activation energy of the conductivity, necessary for calculation of E_{corr} were evaluated from the equation

$$E_x = -R\left[\frac{d \ln \varkappa}{d(1/T)}\right] = \frac{RT^2}{\varkappa}\frac{d\varkappa}{dT} \qquad (12)$$

$$E_x = R\left(\frac{BT^2 + 2CT^3}{A + BT + CT^2}\right) \qquad (13)$$

where A, B, and C are the coefficients of temperature dependence of the conductivity determined in [5]. The values α for investigated melts were taken from the results of density measurements in [8]. The values of $\varkappa$, E_x, E_{corr}, and

Table 1

Values of conductivity, activation energy E_x and E_{corr}, and of the expression $[T/(T - T_0)]^2$ for calculated value of $T_0 = 1404$ K for typical melt with composition 40 mole % $Ca_2MgSi_2O_7$ + 60 mole % $CaSiO_3$

$\dfrac{T}{K}$	$\dfrac{\varkappa}{S\ cm^{-1}}$	$\dfrac{E_x}{kJ\ mol^{-1}}$	$\dfrac{E_{corr}}{kJ\ mol^{-1}}$	$\left(\dfrac{T}{T - T_0}\right)^2$
1673	0.285	166.2	174.9	38.7
1723	0.382	120.3	129.4	29.2
1773	0.471	93.9	103.3	23.1
1823	0.552	76.3	85.9	18.9
1873	0.624	63.3	73.2	15.9
1923	0.687	52.9	63.2	13.7

Fig. 1. Temperature dependence of the conductivity activation energy E_x for melts of the system CaSiO$_3$ (CS)—CaMgSi$_2$O$_6$ (CMS$_2$)—Ca$_2$MgSi$_2$O$_7$ (C$_2$MS$_2$).
1. CS; 2. CMS$_2$; 3. 0.6CMS$_2$ + 0.4C$_2$MS$_2$;
4. 0.3CS + 0.7C$_2$MS$_2$; 5. 0.2CS + 0.8C$_2$MS$_2$;
6. C$_2$MS$_2$.
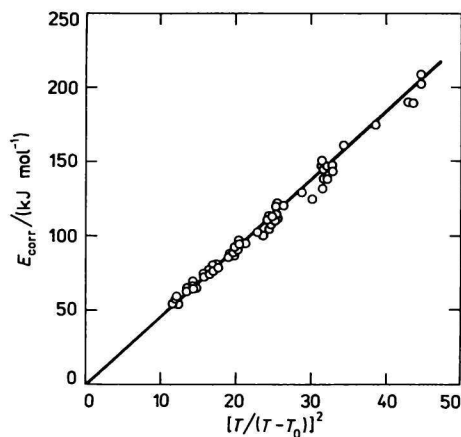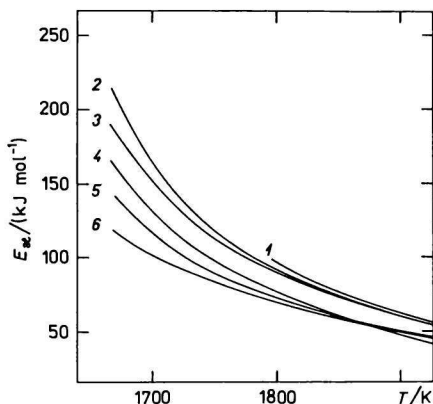
Fig. 2. Dependence E_{corr} vs. $[T/(T - T_0)]^2$ for all investigated melts of the system CaSiO$_3$—CaMgSi$_2$O$_6$—Ca$_2$MgSi$_2$O$_7$.

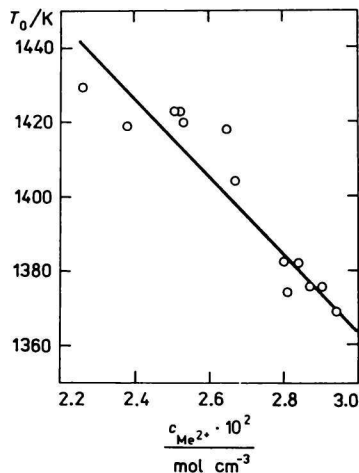
Fig. 3. Calculated values T_0 in terms of concentration of conductive particles in the system CaSiO$_3$—CaMgSi$_2$O$_6$—Ca$_2$MgSi$_2$O$_7$.

$[T/(T - T_0)]^2$ for typical melt with composition 40 mole % Ca$_2$MgSi$_2$O$_7$ + 60 mole % CaSiO$_3$ at various temperatures are listed in Table 1. The temperature dependences of the activation energy of the conductivity for some of the investigated melts are shown in Fig. 1. The verification of the free volume theory according to eqn (11) is demonstrated in Fig. 2.

Discussion

As indicated by Fig. 1 and finally also by eqns *(12)* and *(13)*, the conductivity activation energy of studied melts is strongly temperature dependent. At high temperatures an overlapping of curves occurs, which is probably due to errors of conductivity measurements on this temperature range. Nevertheless, a decrease of the conductivity activation energy with increasing MeO content for given temperature is observed. This fact is in agreement with the results given in [9] though there is a difference in absolute values of activation energies at corresponding temperatures. The difference arises from incorrect method of conductivity cell calibration in [9], which led to measuring of too "steep" temperature dependence of conductivity and thus to higher values of the conductivity activation energy. The problem of conductivity cell calibration has been discussed in [5].

From Fig. 2 it is obvious that within experimental errors the charge transport in the studied melts can be satisfactorily described by the free volume theory in the investigated temperature interval. The value of conductivity is unambiguously determined by the concentration of conductive particles and temperature T_0. According to the free volume theory, T_0 is closely related to transformation temperature. Data referring to transformation temperature of compositions in the CaO—MgO—SiO$_2$ system close to those studied in the present paper are not available in literature.

Calculated values T_0 for investigated samples are introduced in Fig. 3. It was established that temperature T_0 decreases with increasing concentration of conductive particles, *i.e.* with successive destruction of polyanionic network. This is a consequence of the mutual interaction between cations and surrounding SiO$_4$ tetrahedra and results from spatial facilities of close-packed arrangement of atoms in the investigated system, which is essential determining factor for the formation of free volume at T_0. In principle, till now there is not enough information for evaluation of the effect of melt composition on T_0 value. Also reliable values of transformation temperature in alkaline earth metals silicate systems are not available. One of the important factors determining T_0 value should be obviously the degree of polyanion network formation and the bonding force between cations and surrounding SiO$_4$ tetrahedra. In paper [10] T_0 values were found to decrease with increasing concentration of the cations of higher ionic strength in agreement with the results of present study.

· In the present paper the results of the conductivity measurements published by *Kawahara et al.* [11] were interpreted in the same manner. In the corresponding concentration range of the system CaO—MgO—SiO$_2$ T_0 values between 1300 and 1400 K were calculated in agreement with calculations of T_0 from our measurements.

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