

A new model for dielectric relaxation and transport processes in mixed-alkali silicate glasses

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1991 J. Phys.: Condens. Matter 3 623

(<http://iopscience.iop.org/0953-8984/3/5/012>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.151

The article was downloaded on 11/05/2010 at 07:05

Please note that [terms and conditions apply](#).

LETTER TO THE EDITOR

A new model for dielectric relaxation and transport processes in mixed-alkali silicate glasses

A Miotello and L Verdi

Dipartimento di Fisica dell'Università and Consorzio Interuniversitario Nazionale Fisica della Materia, I-38050, Povo (Trento), Italy

Received 14 November 1990

Abstract. We propose a new model for dielectric relaxation in mixed-alkali silicate glasses. The main features of the model are connected with the presence of three different microscopic processes contributing to the dielectric function. These processes are associated both with alkali-alkali static and dynamic correlations. The new model provides the fundamentals of a recently proposed empirical equation for ionic conductivity in mixed-alkali silicate glasses.

Transport and relaxation processes (TRP) in glasses are topics of primary importance in the general field of condensed matter and their understanding is still a matter of considerable effort both from the theoretical and the experimental points of view. The understanding of the microscopic features of TRP in disordered dielectric solids is a paramount problem because of (i) the lack of long range order and (ii) the existence of charge balance problems involved in electronic or ionic transport. In the literature many phenomenological models of structural relaxation have been proposed [1-6], which predict the behaviour of a material in complex situations by generalizing observations derived from simple experiments (see the recent review made by Rekhson [7]). However, as pointed out by Rekhson [7], many problems remain unsolved and controversial. The same general considerations hold for *ab initio* models inquiring into microscopic mechanisms of TRP [8-11].

An almost completely open problem in the science of glass is connected with the huge fall in ionic conductivity when dissimilar monovalent cations are mixed into the glass. This is the mixed-alkali effect.

Up to now a convincing physically meaningful explanation of such an effect seems to be as remote as ever [12] probably also due to the lack of systematic experiments on transport and relaxation phenomena in mixed-alkali glasses.

Recently, starting from general thermodynamic principles, ionic conductivity in mixed-alkali glasses has been formally written [13] as

$$\sigma = \sigma_{ii} + \sigma_{jj} + 2\sigma_{ij}$$

where σ_{ii} and σ_{jj} represent the contribution to the ionic conductivity of ionic species i and j , while σ_{ij} accounts for the role on conductivity of the i - j interaction.

Moreover it was proposed to describe the experimentally observed non-linear scaling behaviour of ionic conductivity (as a function both of temperature T and of the

concentration of different metal alkali species) through the empirical relations [13] for σ_{ii} , σ_{jj} and σ_{ij}

$$\begin{aligned}\sigma_{ii} &= \sigma_0^i \exp\left(-\frac{E_i(2-c_i)}{k_B T}\right) \\ \sigma_{jj} &= \sigma_0^j \exp\left(-\frac{E_j(2-c_j)}{k_B T}\right) \\ \sigma_{ij} &= \sigma_0^{ij} \exp\left(-\frac{E_{ij}}{k_B T}\right)\end{aligned}\quad (1)$$

where $c_{i(j)} = x_{i(j)}/(x_{i(j)} + x_{j(i)})$ and $x_{i(j)}$ is the mole fraction of the $i(j)$ -metal alkali ion.

Notice that when $c_{i(j)} = 1$, i.e. a single alkali species is present, equation (1) still holds [13] and so the conductivities σ_0^i and σ_0^j and the activation energies E_i and E_j are fixed from the knowledge of ionic conductivity (as a function of temperature T) in single alkali glasses.

The empirical equation (1) succeeds in describing the ionic conductivity in many silicate glasses containing different combinations of metal alkali ions i - j and different contents $x_i + x_j$ [13, 14].

In this letter we will provide the fundamentals of empirical equation (1) by proposing a new time-dependent form for $W(t)$, the ionic jumping rate, when metal alkali ions of two different species (say, i and j) are migrating into a dielectric disordered structure and the jumping processes of ion i are correlated both with i and j ions. Starting with this new $W(t)$ function we are able also to provide a new Kohlrausch-type relaxation function for the frequency-dependent dielectric constant in mixed-alkali silicate glasses: this last expression will be verified against some published experimental results.

Since our new proposed expression for the jump rate $W(t)$ stems from some features of the so called coupling model [15, 16], let us briefly recall the main aspects of such a model.

According to the coupling model, an ion starting to jump into a dielectric disordered structure (when other ions are present and long range ion-ion interactions are operating) is initially considered vibrating in a single-particle potential well. Associated with this potential well is the energy barrier E_{a_∞} (see equation (5) below for the meaning of the indices) to the motion of an ion between equivalent sites. The attempt frequency ν_{∞} (see equation (5) below) and the energy barrier E_{a_∞} are called *primitive* (in the coupling model) because these quantities will be modified when interactions between cations and correlations of their motions are considered. In particular in the coupling model it is assumed that the primitive ionic jump rate W_0 is slowed down (by the factor $(\omega_{c_\infty} t)^{-n_\infty}$) by correlation with other ions for times greater than $\omega_{c_\infty}^{-1}$. The frequency ω is introduced in order to determine a time scale on which dynamic correlations become significant.

Now, having in mind these figures of the coupling model, let us elaborate on appropriate $W(t)$ functions for the ionic motion of i and j ions in a dielectric disordered structure when i - j interactions are also operating.

The presence of two different species of metal alkali ions in a dielectric glass suggests in principle the introduction of three different ionic jump rates, namely W_{ii} , W_{jj} , W_{ij} , which, following the *coupling model* [15, 16], we propose to write in the

time-dependent forms

$$W_{ii}(t) = \begin{cases} (W_{0ii})^{1/(1-m_{ii})} & \omega_{cii} t < 1 \\ (W_{0ii})^{1/(1-m_{ii})} (\omega_{cii} t)^{-n_{ii}} & \omega_{cii} t > 1 \end{cases} \quad (2)$$

$$W_{jj}(t) = \begin{cases} (W_{0jj})^{1/(1-m_{jj})} & \omega_{cjj} t < 1 \\ (W_{0jj})^{1/(1-m_{jj})} (\omega_{cjj} t)^{-n_{jj}} & \omega_{cjj} t > 1 \end{cases} \quad (3)$$

$$W_{ij}(t) = \begin{cases} W_{0ij} & \omega_{cij} t < 1 \\ W_{0ij} (\omega_{cij} t)^{-n_{ij}} & \omega_{cij} t > 1 \end{cases} \quad (4)$$

where

$$W_{0\alpha} = \nu_{\infty\alpha} \exp\left(-\frac{E_{a\alpha}}{k_B T}\right) \quad \alpha = ii, jj, ij. \quad (5)$$

The frequencies ω_{cii} , ω_{cjj} and ω_{cij} have been introduced in order to determine a time scale, on which dynamic correlations become significant.

The diagonal $n_{ii(jj)}$ parameters appearing in equations (2) and (3) are linked to the dynamic correlation of $i(j)$ -alkali ions with ions of the same kind [17]. The new off-diagonal term n_{ij} appearing in equation (4) (this equation is essentially devoted to describing the i - j interaction) is due to the relaxation of $i(j)$ -alkali ions in dynamic correlation with those of the $j(i)$ -species.

Notice that we have chosen to write the primitive ionic jump rate $W_{0ii(jj)}$ when passing from a single-alkali glass to a mixed-alkali glass in the form $(W_{0ii(jj)})^{1/(1-m_{ii(jj)})}$.

We call the new introduced parameters m_{ij} and m_{ji} *static correlation coefficients*: they tell us how the energetic configuration of the $i(j)$ -alkali ions is being modified by the presence of the $j(i)$ -alkali ions. We are in principle justified in changing the form of $W_{0ii(jj)}$ in mixed-alkali glasses since, according to the Hendrickson-Bray model [18], each positively charged ion together with the negative charge of its site forms an electric dipole. An interaction energy develops between adjacent metal alkali ions of unequal mass, due to the effect of a local oscillating electric dipole field, created by each ion's vibration [18, 19].

According to our scheme it is clear that m_{ij} and m_{ji} will annihilate themselves when mixed-alkali glass turns single-alkali glass, so as to obtain the expression of $W(t)$ for glasses such as $x\text{A}_2\text{O} : (1-x)\text{SiO}_2$ (where A is an alkali metal).

Once equations (2)–(5) are accepted, three coupled predictions follow as consequences of solutions to the rate equation for the relaxation function $\phi_\alpha(t)$

$$\frac{d\phi_\alpha}{dt} = -W_\alpha(t)\phi_\alpha(t). \quad (6)$$

We discover that the relaxation is simply exponential if $t < \omega_{c\alpha}^{-1}$, whereas for $t > \omega_{c\alpha}^{-1}$ it is stretched exponential (Kohlrausch-type). More particularly, the new relaxation functions which stem from equation (6) have the form

$$\phi_\alpha(t) = \begin{cases} \exp[-(t/\tau_{0\alpha})] & \omega_{c\alpha} t < 1 \\ \exp[-(t/\tau_\alpha)^{1-n_\alpha}] & \omega_{c\alpha} t > 1 \end{cases} \quad (7)$$

where

$$\tau_{ii(jj)} = \left[(1 - n_{ii(jj)}) \omega_{c_{ii(jj)}}^{n_{ii(jj)}} \tau_{0_{ii(jj)}}^{1/(1-m_{ij(ji)})} \right]^{1/(1-n_{ii(jj)})} \quad (8)$$

$$\tau_{ij} = \left[(1 - n_{ij}) \omega_{c_{ij}}^{n_{ij}} \tau_{0_{ij}} \right]^{1/(1-n_{ij})} \quad (9)$$

$$\tau_{0_{ii(jj)}} = \frac{1}{W_{0_{ii(jj)}}} \quad \tau_{0_{ij}} = \frac{1}{W_{0_{ij}}} \quad (10)$$

Now starting from the $\phi_\alpha(t)$ and knowing that the DC conductivity is given by [20]

$$\sigma_{DC_\alpha} \equiv \sigma_\alpha = \epsilon_0 \epsilon_{\infty_\alpha} \left(\int \phi_\alpha(t) dt \right)^{-1} \quad (11)$$

(where ϵ_0 is the permittivity of free space) and bearing in mind equations (5), (8) and (9), we find

$$\begin{aligned} \sigma_{ii} &= \sigma_{0_{ii}} \exp \left(- \frac{E_{a_{ii}}}{(1 - n_{ii})(1 - m_{ij})k_B T} \right) \\ \sigma_{jj} &= \sigma_{0_{jj}} \exp \left(- \frac{E_{a_{jj}}}{(1 - n_{jj})(1 - m_{ji})k_B T} \right) \\ \sigma_{ij} &= \sigma_{0_{ij}} \exp \left(- \frac{E_{a_{ij}}}{(1 - n_{ij})k_B T} \right) \end{aligned} \quad (12)$$

This formula is identical to the empirical one proposed by Miotello and Mazzoldi [13] if we identify the diagonal and off-diagonal terms through the relations

$$E_{a_\alpha} = E_{a_\alpha}^* (1 - n_\alpha) \quad (13)$$

$$2 - c_{i(j)} = \frac{1}{1 - m_{ij(ji)}} \quad (14)$$

Relation (13) is none other than one of the consequences of the coupling model [17], $E_{a_\alpha}^*$ being the activation energy for the DC conduction process connected with the primitive energy barrier through the factor $(1 - n_\alpha)$. As to the new relation (14), notice first of all that this relation allows us to test the self-consistency of model proposed for the relaxation. Indeed from this formula follows that $m_{ij(ji)}$ will annihilate itself, when the $j(i)$ -alkali is absent ($c_{i(j)} = 1$), and moreover $W_{ii(jj)}(t)$ will reduce itself to the form it has in single-alkali glasses.

In addition notice that this relation also tells us that $m_{ij(ji)}$ lies between 0 and $\frac{1}{2}$.

Now let us look at some different kinds of experimental results which support our new proposal concerning the $W(t)$ functions as well as the equations derived from these new time dependent jumping rates.

First of all notice that from equation (5) the presence of a second alkali species (say, j) increases the attempt frequency $\nu_{\infty_{ii}}$ of an i -alkali to $(\nu_{\infty_{ii}})^{1/(1-m_{ij})}$; this very fact is experimentally observed, e.g., in studies of diffusion coefficients (as defined by

Fick's law) in mixed-alkali glasses. Indeed the frequency factor D_0 of a metal alkali ion is observed to increase when passing from a single-alkali glass [21] to a mixed-alkali one [22].

Moreover the new relaxation functions (equation (7)), derived above for mixed-alkali glasses, allow us to establish, within the framework of the linear response theory, a new expression for the dielectric function $\epsilon(\omega)$. In particular, in connection with three distinct processes (equations (2)–(5)) in the ionic relaxation in mixed-alkali glasses, the dielectric function will assume the form of a three-term sum [8]:

$$\epsilon(\omega) = \sum_{\alpha} \left[\epsilon_{\infty_{\alpha}} + (\epsilon_{S_{\alpha}} - \epsilon_{\infty_{\alpha}}) \int_0^{\infty} \exp(-i\omega t) \left(-\frac{d\phi_{\alpha}(t)}{dt} \right) dt \right]. \quad (15)$$

To check the validity of equation (15) it would be important to fit such an equation against experimental results for, e.g., the imaginary part, ϵ'' , of the dielectric function in mixed-alkali glasses when both temperature and $x_i + x_j$ values are systematically varied. Moreover, for a chosen $x_i + x_j$ value it would be important to know the corresponding ionic conductivity to test the validity of equation (13). Generally it is not possible to find, all together, in the current glass literature, the experimental results quoted above and so we restricted our test of equation (15) to the 0.15Li₂O : 0.15K₂O : 0.70SiO₂ and 0.20Li₂O : 0.10K₂O : 0.70SiO₂ glasses, for which we have appropriate data for several properties [23].

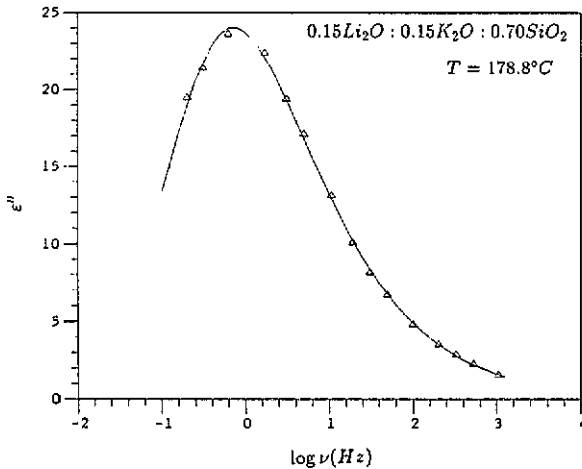


Figure 1. Plot of the imaginary part of the dielectric constant against $\log \nu$ in 0.15Li₂O : 0.15K₂O : 0.70SiO₂ glass. The triangles represent the experimental data [23] and the full curve is computed from the model described in text.

In figures 1 and 2 we report along with the experimental data (triangles) the theoretical results obtained with the imaginary part of (15). By minimizing the χ^2 -value we have determined the parameters $\epsilon_{S_{\alpha}} - \epsilon_{\infty_{\alpha}}$ ($\epsilon_{S_{\alpha}}$ and $\epsilon_{\infty_{\alpha}}$ are the low- and high-frequency dielectric constants, respectively), n_{α} and τ_{α} .

Notice that for simplicity we report ϵ'' against $\log \nu$, ($\omega = 2\pi\nu$) at only one temperature for the two mixed-alkali glasses considered. However, we have analysed the experimental data [23] for all the available temperatures, in all cases performing the χ^2 -test: this always gives good results, the Q -probability being > 0.5 .

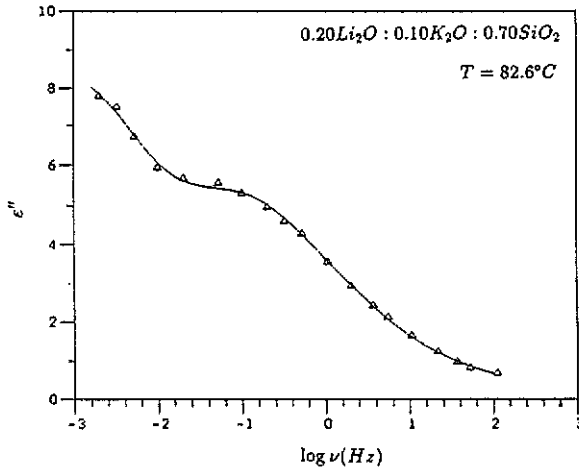


Figure 2. Plot of the imaginary part of the dielectric constant against $\log \nu$ in 0.20Li₂O : 0.10K₂O : 0.70SiO₂ glass. The triangles represent the experimental data [23] and the full curve is computed from the model described in text.

In the first case, when $x_i = x_j$, (figure 1) only a single relaxation process has been discovered, which is characterized by an activation energy (determined analysing ϵ'' at all available temperatures [23]) $E_a^* \approx 1.52$ eV. This may be attributed to the off-diagonal term (equation (9)). At this point it is very important to underline that also in ionic transport when $x_i \approx x_j$ only the σ_{ij} term is relevant and characterized by an high activation energy [13, 14].

In the second case, $x_i \neq x_j$, (figure 2) there are three different relaxation processes: two of them ($E_{a_i}^* \approx 0.85$, $E_{a_j}^* \approx 0.95$) may be associated with the alkalis separately (equation (8)), while the third one may be attributed to the i - j coupled relaxation (equation (9)) with activation energy $E_a^* \approx 1.45$ eV.

Notice that the energetic features emerging from these fittings are consistent (equation (13)) with the ones coming out from independent measurements of ionic conductivities [13, 14]. We are aware that in fitting the experimental data of ϵ'' against $\log \nu$ with the imaginary part of equation (15), we employed a large number of adjustable parameters (associated, however, with the many physical microscopic processes involved in ionic relaxation in mixed-alkali glasses) but it is comforting to note that the χ^2 -test provides good results in any case.

Thus the experimental results at our disposal, both on diffusion and relaxation processes, emphasize the validity of our new proposed model for ionic relaxation in mixed-alkali glasses.

Nevertheless, to prove definitely our new model for TRP in mixed-alkali glasses, it would be important to make:

(i) a detailed experimental analysis of $\epsilon''(\omega)$ over a larger frequency range (varying the masses of the two metal alkali ions systematically), in order to point out directly a three-peak structure in $\epsilon''(\omega)$;

(ii) a systematic analysis of the dielectric relaxation and ionic conductivity in mixed-alkali glasses varying both c_i and c_j , and $(x_i + x_j)$, in order to prove equation (14) specifically;

(iii) a computer simulation of the new attempt frequencies appearing for two differ-

ent masses randomly distributed in a dielectric disordered structure, when long-range ion-ion (and dipole-dipole) interactions are operating.

In conclusion, we think that our proposed model for TRP in mixed-alkali glasses opens a new way for a better understanding of the physics of disordered dielectric solids, suggesting also some new systematic experiments on relaxation processes in mixed-alkali glasses.

References

- [1] Rendell R W, Ngai K L, Fong G R and Aklonis J J 1987 *Macromolecules* **20** 1070
- [2] Davies R O and Jones G O 1953 *Proc. R. Soc. A* **217** 26
- [3] Gupta P K and Moynihan C T 1976 *J. Chem. Phys.* **65** 4136
- [4] Berg J I and Cooper A R Jr. 1978 *J. Chem. Phys.* **68** 4481
- [5] Lesikar A V and Moynihan C T 1980 *J. Chem. Phys.* **73** 1932
- [6] Gupta P K 1983 *Lectures on Glassy State* (Case Western Reserve University); 1986 Fictive pressure effects in relaxation (paper 10-BEG-86F) *Ceram. Bull.* **65** 1363
- [7] Rekhson S 1987 *J. Non-Cryst. Solids* **95-96** 131
- [8] Jonscher A K 1983 *Dielectric Relaxation in Solids* (London: Chelsea Dielectrics Press)
- [9] Adam G and Gibbs J H 1965 *J. Chem. Phys.* **43** 139
- [10] Sherer G W 1984 *J. Am. Ceram. Soc.* **67** 504; 1986 **69** 374
- [11] Fredrickson G H and Brawer S 1986 *J. Chem. Phys.* **84** 3351
- [12] Tomandl G and Schaeffer H A 1985 *J. Non-Cryst. Solids* **73** 179 and references therein
- [13] Miotello A and Mazzoldi P 1987 *J. Non-Cryst. Solids* **94** 181
- [14] De Marchi G, Mazzoldi P and Miotello A 1988 *J. Non-Cryst. Solids* **104** 211; notice that $c_{i(j)}$ of equation (1) corresponds to $n_{i(j)}$ of ref [3].
- [15] Ngai K L, Rendell R W, Rajagopal A K and Teitler S 1986 *Ann. NY Acad. Sci.* **484** 150 and references therein; 1986 *IEEE Trans. Electron. Insul.* **EI-21** 313
- [16] Ngai K L, Rajagopal A K and Teitler S 1988 *J. Chem. Phys.* **88** 8 5086
- [17] Ngai K L, Mundy J N, Jain H, Kanert O and Balzer-Jollenbeck G 1989 *Phys. Rev. B* **39** 6169
- [18] Hendrickson J R and Bray P Y 1972 *Phys. Chem. Glasses* **13** 43, 107
- [19] Dietzel A M 1983 *Phys. Chem. Glasses* **24** 172
- [20] Isard J O 1988 *Sol. State Ionics* **31** 187
- [21] Frischat G H 1975 *Ionic Diffusion in Oxide Glasses* (Bay Village, OH: Trans. Tech. Publications)
- [22] McVay G L and Day D E 1970 *J. Am. Ceram. Soc.* **53** 508
- [23] Namikawa H 1974 *J. Non-Cryst. Solids* **14** 88