THE MODEL OF ELECTRICAL CONDUCTIVITY AND DIFFUSION IN GLASSES WITH ACCOUNT FOR THEIR STRUCTURAL FEATURES

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The authors propose two ways to value the influence of alkali-silica glass structure on its electrical characteristics and alkaline cation diffusion ratio: drop model of liquative inhomogeneous alkali-silica glass structure description (in no liquation conditions), and homogeneous structure model with even distribution of alkaline cations.

In the 1st case the inhomogeneous conducting medium is a homogeneous matrix of constant composition with dispersed spherical drops with another content of alkaline oxide (dispersed phase). All diversity of sizes and possible spacing of the drops is substituted by a mean radius of drop δ and a mean spacing of the centers of drops $2R$. Then one can draw an average sphere with radius R from the center of each average drop. It is clear, that the electrical parameters of the medium depend on the electrical conductivity of parts of the orb, with the effective electrical conductivity of the ball equal to average electrical conductivity of the medium.

D. Maxwell has solved the problem of the effective resistance of an inhomogeneous ball [1, p. 353], and the solution presented in the terms of conductivity and the recognized specifications looks like:

$$\sigma = \sigma_1\left(1 + \frac{u}{1/(p-1) + (1-u)/3}\right) = \sigma_1 \varphi(u, p),$$

(1)

where $u = (\delta/R)^3$, $p = \sigma_2/\sigma_1$, and σ, σ_1 and σ_2 are the electrical conductivity values: σ – of the medium, σ_1 – of external $(\delta \leq r \leq R)$ and σ_2 – of internal $(r < \delta)$ parts of the ball. Thus, parameter u shows the volume fraction of dispersed phase with electrical conductivity σ_2.

In agreement with the authors [2, 3], changes in the gross (i.e., volume averaged) composition of glass are accompanied by redistribution of the matrix and dispersed phase volume fractions without changing their inner phase composition, thus the u parameter can vary in certain ranged of compositions at the invariable p parameter value. Glasses of the same system with varied compositions can have several ranges with this feature, depending on quantity of mostly possible composition phases realized in the given system.

We can consider with adequate accuracy, that:

$$u = (c-c_1)/(c_2-c_1),$$

where c and c_i are weight concentrations of alkaline oxide: c – volume averaged, c_1 - in the matrix, c_2 - in the dispersed phase. As usually the electrical conductivity measurement results are recorded on the logarithm scale, we shall put it instead of (1) as:

$$lg\sigma = lg\sigma_1 + lg\varphi(u,p) \qquad (2)$$

The $p > 1$ case describes a system, containing low-conductivity matrix with high-conductivity inclusions. The increase of alkaline oxide in glass leads to linear growth of u parameter and a faster growth of $lg\varphi(u)$. In $p < 1$ case the matrix has increased conductivity, and the growth of u parameter is accompanied by more or less sharp (depending on p parameter value) decrease of $lg\varphi(u)$ value. At that, the growth of u parameter means the decrease of $c.$

As the connection between c and u in both cases is linear, the reciprocal positioning of high - and low conductive phases is possible via analyzing singular points on $lg\sigma$ from c relationship curve. If the curve has points of fracture, where $lg\sigma(c)$ curve slope changes by jump, such points can be considered as boundaries of the sectors with different p values. If the sign of curvature also changes at the boundary (i.e. the point of fracture is also the inflection point), the reciprocal positioning of high- and low-conductive phases change.

The results of applying of this model to lithium- and sodium-silica glasses are seen on fig. 1 and 2.
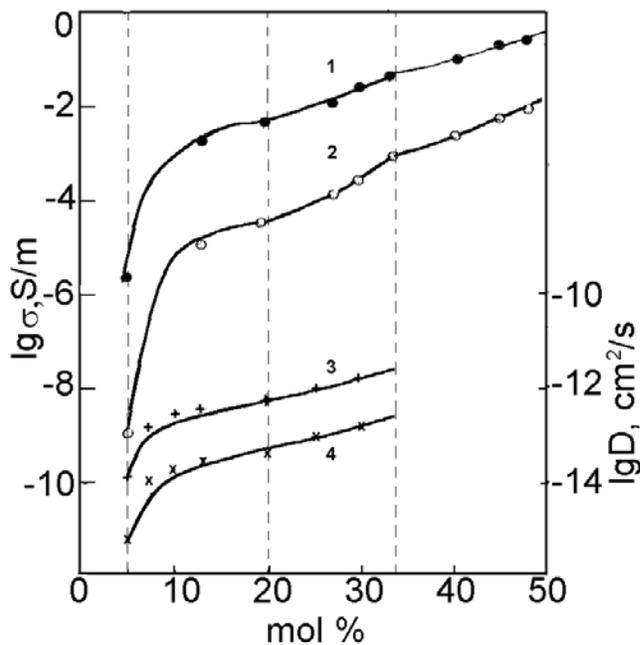

The whole range of alkali-silica glass compositions can be divided into three sectors by the character of experimental relationship (on the figures they are separated by vertical touched lines). The appearance of $lg\sigma$ from Na_2O concentration relationship allows suspecting, that in the first sector of this range of compositions the low-conductive phase is isolated. For the sectors II and III the low-conductive phase forms the matrix, with sector II this phase corresponded to compositions with 20 Mol% alkaline oxides, and with sector III – to a disilica. Ideally, the glass composition shall be homogenous at boundary values of 20 and 33.3 Mol%.

Fig. 1. Electrical conductivity and diffusion ratios of Na_2O-SiO_2 glasses: lgσ: 1 - t=300^{0}C; 2 - t=150^{0}C [4, p. 274]; lgD: 3 - t=415^{0}C; 4 - t=300^{0}C [5].

Table 1 shows the parameters values used for calculating the electrical conductivity of sodium- and lithium-silica glasses for figures 1 and 2.

It is visible, that the calculated curves give a satisfactory description of experimental relations obtained by different authors.

The study [2] compares electrical characteristics of lithium-silica glasses with the same composition, but different thermal history: one were fast chilled (hardened) right after cooking, the others were subjected to annealing, while practically all annealed samples showed lower values of electrical conductivity than the hardened.
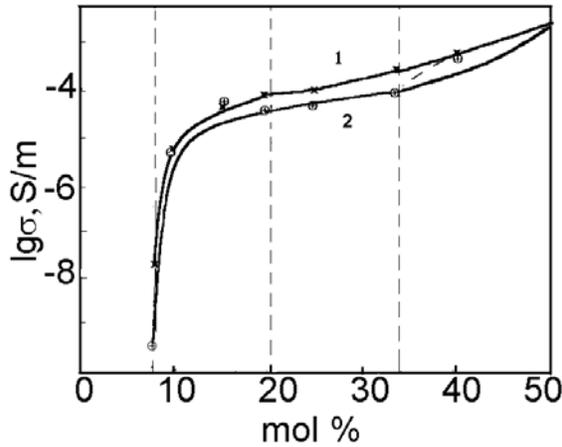
Fig. 2. Electrical conductivity of Li_2O-SiO_2 glasses after different heat treatment at t=150°C [2]:1 - hardened; 2 - the annealed.

The values obtained for sector III compositions allow for dual interpretation, what is marked in the picture by a stroked line, and in the table – by brackets.

Table 1

Na_2O-SiO_2	O.A. Mazurin [4, p.274]			Li_2O-SiO_2	V.Leko [2]		
sector boundaries Mol %	$t,^0C$	$\lg\sigma_1, S/m$	p	sector boundaries Mol %	$t=150^0C$	$\lg\sigma_1, S/m$	p
I	150	-4,45	10^{-4}	I	hardened	-4,11	$2,0\cdot10^{-4}$
5 - 20	300	-2,36	10^{-3}	8 - 20	annealed	-4,32	$6,5\cdot10^{-6}$
II	150	-4,45	24,5	II	hardened	-4,11	4,0
20 -33.3	300	-2,36	5,2	20 -33.3	annealed	-4,32	2,1
III	150	-3,06	13,2	III	hardened	-3,52	12,7
33,3-50	300	-1,34	8,7	33,3-50	annealed	-4,00	26
						(-2,60)	(0,038)

As the electric conductivity in sodium-silica glasses is determined by the alkaline cation mobility, and the latter influences the said cation diffusion, we can expect similar relation between the cation diffusion ratio and glass composition. See Fig. 1 for the relations between *lgD* and composition at two temperature values [5], and the table 2 – for the parameter values, used calculating the curves.

The Figure shows, that the general changing of *lgD* together with changing the glass composition repeats the similar relation, as shown for *lgσ*.

Table 2

sector boundaries	$t,^0C$	lgD_1, м²/c	p
I	300	-13,30	0,018
4 -20 Mol%	415	-12,23	0,030
II	300	-13,30	4,5
20 - 33,3 Mol%	415	-12,23	4,0

Thus, this model shows that in the studied structures a dispersed phase is low-alkaline in glasses with less than 20 Mol% of alkaline oxide, and high-alkaline - in glasses with high gross content of alkaline oxide.

It does not contradict to the interpretation in [2,3], since consider no-liquation conditions.

The comparison of electrical conductivity in glasses, with compositions matching the sector boundaries (see Table 1) proves that the sharp relation between electrical conductivity and composition remains and for homogeneous structures too. This can be apparently explained by the nature of medium, surrounding

cation in alkali-silica glasses. The confirmation to that is a relation between electrical conductivity and composition of alkali-silica glasses, not tended to liquation and considered as homogeneous, such as potassium, rubidium and cesium glasses.

The relation between these glasses' electrical conductivity logarithm and mean spacing of cations L (fig.3) is equal to:

$$\sigma = \sigma_L e^{-\alpha L} \text{,} \tag{3}$$

where σ_L and α do not depend on L, but are subject to change together with the temperature.
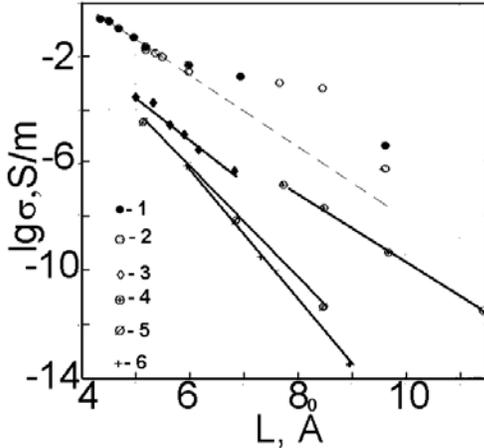
The similar formula comes out from the theory of electron conduction in no crystalline medium [6], when the conductivity depends on the presence of impurity centers located on the mean distance of L from each other. As conductivity in the considered glasses is only ionic, the exponential factor in (3) can be estimated as an efficiency ratio of phonon interplay of the centers, formed by alkaline oxide cations. The result of such interplay is the cation activation for its participation in transfer processes - electrical conductivity or diffusion.

Fig. 3 Relation between the electrical conductivity and mean spacing of cations in alkaline-silica glasses: $Na_2O - SiO_2$, 300^0C: 1 - [7]; 2 - [4, p. 280]; $K_2O - SiO_2$, 150^0C: 3 - [4, p. 330]; 4. - [4, p. 332]; 5. $Rb_2O - SiO_2$, 100^0C, [4, .p. 348]; 6. $Cs_2O - SiO_2$, 100^0C, [4, p. 356]

The glasses, capable of liquation, apparently obey to this regularity, though only in case of uniform distribution of cations in the volume.

This relation for sodium-silica glasses is shown in Fig. 3 in strokes. For low-sodium glasses (sector I on Fig. 1) the deviation from linear dependence is determined by preferential influence of non-homogenous structure of glasses with these compositions, and for middle- and high-sodium glasses the role of non-homogeneity is negligible.

As far as electrical conductivity is an activation process, the temperature relation is usually presented as:

$$\sigma = \sigma_0 e^{-E/RT} \text{,}$$

where E depends on the cation nature and its concentration in glass, while when considering the (3) the dependence from L should be linear:

$$E = E_0 + \beta L$$

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