Correlation between floppy to rigid transitions and non-Arrhenius conductivity in glasses

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Non-Arrhenius behaviour and fast increase of the ionic conductivity is observed for a number of potassium silicate glasses \((1-x)SiO_2 - xK_2O\) with potassium oxide concentration larger than a certain value \(x = x_c = 0.14\). Recovery of Arrhenius behaviour is provided by the annealing that enhances densification. Conductivity furthermore obeys a percolation law with the same critical concentration \(x_c\). These various results are the manifestation of the floppy or rigid nature of the network and can be analyzed with constraint theory. They underscore the key role played by network rigidity for the understanding of conduction and saturation effects in glassy electrolytes.

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Amorphous electrolytes are a class of materials where cationic or anionic sites are not confined on a specific lattice but are essentially free to move throughout the structure. Among those, oxide and chalcogenide fast ionic conducting (FIC) glasses show high electrical conductivities [1,2] with potential applications for solid state batteries, sensors and displays. Recent studies have indeed shown that the dc conductivity of certain classes of sulphide systems at room temperature could be increased [3,4] up to \(10^{-2}\Omega^{-1}\cdot cm^{-1}\). Active research is therefore undertaken to make these superionic glasses even more conductive. A natural question that emerges deals with the upper conduction limit that could be reached for these systems as saturation effects [5] and departure from Arrhenius behaviour (AB) in conductivity with increasing temperature have been found to occur. Alternatively, one may wonder what kind of chemical elements should be used to avoid the latter. It is generally accepted that both structural and conduction energetic features are involved in the mechanism of superionic conductors and various studies have highlighted the role played either by carrier concentration [6], mobility or temperature [7]. Others have emphasized the influence of the dynamics [8] or the composition [9] of these peculiar materials to understand their surprisingly high values of conductivity. A basic question is therefore to understand what produces the limitation in conductivity [10].

From the measurements realized on potassium silicates \((1-x)SiO_2 - xK_2O\), we suggest in this Letter that the electrical transport follows percolative behaviour with alkali concentration and leads to a fast increase of the dc conductivity for \(x > x_c = 0.14\). The latter critical concentration furthermore separates glasses with AB from those displaying non-AB. We show that annealing and densification of these electrolytes tends to reduce the saturation and that densification with annealing may be responsible for the loss of non-Arrhenius variation. Finally, we suggest that there is a common mechanical origin for the observation of carrier mobility percolation, saturation effects and densification that can be derived directly from the Phillips-Thorpe constraint theory [11]. Glasses with \(x < x_c\) are found to be intrinsically stressed rigid and display AB while those with \(x > x_c\) are floppy and show saturation effects and non-AB. Thus non-AB electrical behaviour intervenes only in floppy glasses. The trends measured here and the critical composition observed correlate with constraint counting algorithms applied on the local structure of the glass. This links for the first the elastic nature (floppy, rigid) of the glass network via its structure, to ionic conductivity and ease of conduction.

The glasses were prepared by melting a mixture of \(SiO_2\) and \(KHCO_3\) powders in a platinum crucible (200 g batch) at 1500 – 1600°C for 4 hours and were then quenched on a stainless steel. The annealed glasses were obtained by heating the as-quenched melt (termed in the following as virgin) at temperatures close to \(T_g\) for 4 hours followed by a slow cooling down to room temperature. The complex electrical conductivity was measured on Pt-metallized discs (1mm thickness and 12 mm diameter) using a Solartron SI 1260 impedancemeter in the frequency range 1Hz-1MHz from room temperature up to \(T_g + 60^°C\). The mass densities of virgin and annealed glasses were measured by buoyancy method with an accuracy of 0.001 g/cm³.

Figure 1 shows the Arrhenius plots of the ionic conductivity for the different virgin potassium silicates. One can first observe that glasses at low potassium concentration (e.g. \(x = 0.05\)) display an almost perfect Arrhenius behaviour \(\sigma T = \sigma_0\exp[-E_A/RT]\) with respect to the temperature while those at high concentration exhibit a clear saturation manifested by a significant curvature at high temperatures that signals departure from Arrhenius
The present observation has been already reported for a variety of solid electrolytes, and it was concluded [5] that ion-ion interactions can be responsible for the latter anomalous behaviour. If this would be the case, one would expect to see the saturation emerge in potassium silicates only in the high alkali limit where the proliferation of non-bridging anions makes this scenario plausible. Apparently, this seems in contradiction with our results that show already non-Arrhenius behaviour for the $x = 0.17$ composition. For the latter, $Q^3 - Q^3$ bondings that could potentially lead to ion-ion interactions are absent [12] at this concentration. $Q^3$ denotes here a basic $SiO_{4/2}$ tetrahedron having $4 - n$ non-bridging oxygens that are only bonded to a potassium cation.

The insert of Figure 1 highlights the fact that annealing removes the curvature and brings the conductivity in the glass to Arrhenius behaviour even though the absolute value of conductivity decreases with respect to the virgin state. This is a feature that has been observed long time ago by Ingram and co-workers [13] for oxysalt chalcogenides involving iodine anions and identified with the dynamic temperature dependent restructuring I-sublattice. Densification was claimed to play the key role and it appears that this is also the case in the present system as density changes with annealing are relatively small (Figure 3a) for compositions where no departure from Arrhenius behaviour is seen. This is also in agreement with the fact that decrease of density increases conductivity [14] in fast ion conducting glasses.

Figure 2 shows for two virgin and two annealed potassium glasses ($x = 0.05$ and $0.17$) the apparent activation energy that is computed as the running slope between adjacent temperature conductivity data points. We note from the figure that in the case of the latter virgin glass, the difference in activation energy between the low and the high temperature side is about $0.4 \, eV$ ($0.7eV$ at $T \simeq 400$ $K$ i.e. $10^3/T$ $\simeq 2.5$), and $0.3 \, eV$ at $T \simeq 700$ $K$ i.e. $10^3/T$ $\simeq 1.4$) which is of the order of the low temperature activation energy itself. For comparison, the corresponding reported difference [5] for the highest saturated silver superconducting chalcogenide was about $0.15 \, eV$. The effect of saturation is therefore certainly not weak and does not appear to be restricted to chalcogenides [5]. On the other hand, both virgin and annealed ($x = 0.05$) glasses display a more or less constant activation energy (respectively found as $1.04 \, eV$ and $0.93 \, eV$) in harmony with the observed Arrhenius trend in the insert of Fig. 1. From the observations made on both figures, it becomes clear that a dramatic change in regime occurs in the composition intervall $0.12 < x < 0.17$. This change is also observable from the low temperature activation energy difference between the annealed and virgin state $\Delta E_A = E_A(\text{anneal.}) - E_A(\text{virg.})$ which displays (Fig. 3a) a significant drop in the aforementioned compositional interval.

Lagrange bonding constraint counting (LBCC) that include bond stretching and bond-bending forces, appear to be helpful [11] in understanding the modification of the electrical properties with potassium concentration. Connections of network rigidity with electrical conduction in solid electrolytes has been established [18] recently.
LBCC is also a systematic tool to correlate quantitatively network modification with the glass-forming tendency in chalcogenide [19] and oxide glasses [20] and provides the framework to understand the reported results. The present system can be seen as composed of a network of N atoms among which \( N_f \) are r-fold coordinated. The enumeration of mechanical constraints leads to \( r/2 \) bond stretching constraints for an r-fold atom while there are \( 2r - 3 \) bond bending constraints [21]. The constraints acting on the terminal potassium cation and the related non-bridging oxygen are handled as described in Ref. [22] where broken constraints are considered.

According to this enumeration, a mean-field rigidity transition is expected to occur [21] when the number of zero frequency (floppy) modes \( f \) vanishes which happens when the number of constraints per atom \( n_c = 5r/2 - 3 \) equals the number of degrees of freedom par atom \( N_f = 3 \) in three dimensions. In silicates, such a transition occurs at the alkali concentration of \( x = 0.20 \) when the cation size is small [20]. Due to the potassium cation size (cation radius \( R_{K+} = 1.33 \) Å and \( R_{Na+} = 0.95 \) Å, [23]), one expects that a supplementary oxygen angular constraint is broken because the bridging bond angle \( Si-O-Si \) in the glass network is found to display wide excursions (135–155°) around a mean angle that is much larger [24] than in the sodium analog [25]. According to this enumeration, a rigid to floppy transition is predicted [26] at the concentration of \( x_c = 0.14(3) \), close to the observed threshold observed in Fig. 3a. The study of the local structure of potassium silicate glasses obtained from NMR investigation provides a supplementary evidence [16] about the location of the rigid to floppy transition because constraint counting can be applied onto the observed \( Q^n \) speciation to yield the probability of finding stressed rigid and floppy structures in the network (Figure 3b). Furthermore, we notice that a cluster composed of a \( Q^4 \) and \( Q^3 \) tetrahedron (a “K\( _2 \)Si\( _3 \)O\( _4 \)” like cluster) is optimally constrained (isostatically rigid, satisfying \( n_c = 3 \)) [17] and the corresponding probability of finding the latter is found to be maximum [16] around the same critical concentration of \( x_c = 0.14 \). Thus at this composition the network is mainly stress free. For larger concentrations, SICA predicts the growing emergence of floppy clusters such as \( Q^3 - Q^4 \) bondings.

In a stressed rigid glass, the mobility of the potassium atoms should be rather weak because the cations have to overcome a strong mechanical deformation energy to create a ”doorway” that allows to move from one anionic site to another. With the softening of the glass structure produced by the addition of potassium oxide, one expects that this energy decreases with x. For instance, in the strong electrolyte Anderson-Stuart model [29], the activation energy for conductivity \( E_A = E_c + E_m \) depends on a Coulombic term \( E_c \) controlling the free carrier rate and a strain term \( E_m \) that contribute to the carrier mobility. The latter can be thought as the energy required to enlarge the radius of an anionic site perpendicular to the ”doorway” direction of cation displacement. It is thus proportional [30] to the elastic constant \( c_{44} \).

In an ideal floppy glass for which \( x > x_c \), this strain energy is zero as the related elastic constants \( (c_{11}, c_{44}) \) are found to vanish when \( f = 0 \) (or \( x = x_c \)) [27,28]. This should lead to an enhancement of mobility and percolation of floppiness should equal to percolation of potassium mobility, producing the substantial increase of conductivity seen on Figure 4. Onset of conductivity in the annealed glasses furthermore follows a site percolation law [31] of the form: \( \sigma(x)/\sigma_0 = (x - x_c)^\mu \) that is valid.

FIG. 3. a) Low temperature activation energy difference \( \Delta E_A \) (open circles) between the virgin and annealed samples, together with previous results obtained (filled circles, [15]), as a function of potassium concentration x. Right axis shows the corresponding density change \( \Delta \rho \) (open triangles) with annealing. b) Relative fraction of \( Q^{4-3} \) units (filled circles, from [16]) together with theoretical prediction of the probability of \( Q^{4-3} \) units (dotted line) computed from size increasing cluster approximations (SICA) [17]. The solid lines represent the probability of finding stressed rigid, isostatically rigid and floppy clusters. The lower horizontal axis is scaled in atomic number of floppy modes \( f \). The vertical broken line corresponds to the mean-field rigidity transition \( x_c = 0.14 \) where \( f = 0 \).
for random or periodic arrays (Insert of Figure 4), with powers ranging between $p = 1.77$ at 200°C and 1.09 at 400°C. Recently a clear experimental correspondence between a previously reported conductivity threshold composition [32] and the rigidity transition composition has been established [33] for silver phosphate glasses.

![Figure 4](image)

**FIG. 4.** Conductivity of annealed $(1-x)\text{SiO}_2-x\text{K}_2\text{O}$ glasses for various temperatures. The insert shows the corresponding logarithmic plot against $\log(x-x_c)$. Dotted lines in the insert are the power-law fits.

In summary, we have shown that saturation effects and non-Arrhenius behaviour were taking place in the high temperature limit of only certain potassium silicates at compositions where the network is floppy. We have pointed out that there was also a clear correlation between the onset of conductivity or mobility, effect of annealing and the elastic nature of the host network, stressed rigid or floppy. We believe that these new connections will bring insights and understanding for the improvement of amorphous fast ion conductors.

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