Correlation between Floppy to Rigid Transitions and Non-Arrhenius Conductivity in Glasses

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Non-Arrhenius behavior is observed for a number of virgin potassium silicate glasses $(1-x)\mathrm{SiO}_2 - x\mathrm{K}_2\mathrm{O}$ with a potassium oxide concentration larger than a certain value $x = x_c = 0.14$. Recovering of Arrhenius behavior is provided by the annealing that enhances densification. These various results are the manifestation of the floppy or rigid nature of the network. Compositional effects and saturation with temperature can be analyzed with a combination of constraint theory and a point defect model. 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 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 $10^{-2}\ \Omega^{-1}\,\mathrm{cm}^{-1}$. 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 behavior (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], the presence of point defects [9] or the composition [10] 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 [11].

From the measurements realized on potassium silicates $(1-x)\mathrm{SiO}_2 - x\mathrm{K}_2\mathrm{O}$, we show in this Letter that a certain critical alkali concentration $x_c = 0.14$ 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 saturation effects and densification that can be derived directly from the Phillips-Thorpe constraint theory [12]. 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 electrical non-AB intervenes only in virgin 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 time 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 h 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 h followed by a slow cooling down to room temperature. The complex electrical conductivity was measured on Pt-metallized discs (1 mm thickness and 12 mm diameter) using a Solartron SI 1260 impedance meter in the frequency range 1 Hz–1 MHz from room temperature up to $T_g + 50\,^\circ\mathrm{C}$. The accuracy of the measurement was estimated to be of ± 0.2 in $\ln \sigma T$ units. The mass densities of virgin and annealed glasses were measured by buoyancy method with an accuracy of $0.001\ \mathrm{g/cm^3}$.

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 behavior $\sigma T = \sigma_0 \exp[-E_A/RT]$ 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 behavior.

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

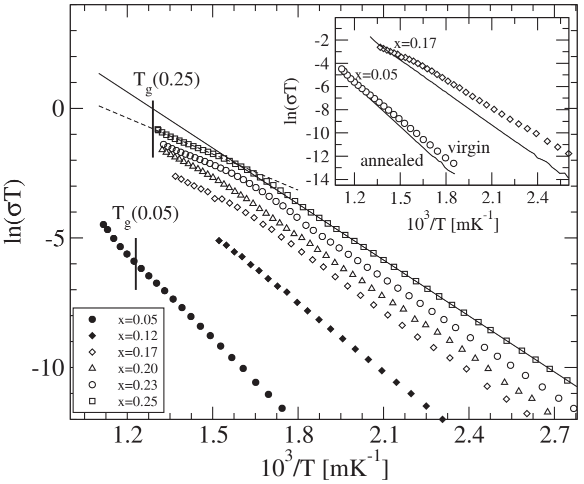

FIG. 1. Arrhenius plots of virgin potassium silicate glasses with changing potassium oxide concentration x. The solid line corresponds to a low-temperature Arrhenius fit for the $x = 0.25$ composition. The inset shows the effect of the annealing on the conductivity for two glass compositions. Conductivity of virgin glasses: $x = 0.05$ (open circles) and $x = 0.17$ (open diamonds) compared to that of the annealed glasses (solid lines). The vertical lines serve to indicate the T_g for two compositions (0.05 and 0.25). The broken line is used in the discussion (see text for details).

anomalous behavior. 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 nonbridging anions makes this scenario plausible. Apparently, this seems in contradiction with our results that show non-Arrhenius behavior already for the $x = 0.17$ composition. For the latter, Q^3-Q^3 bondings that could potentially lead to ion-ion interactions [13] are absent [14] at this concentration. Q^n denotes here a basic $SiO_{4/2}$ tetrahedron having $4 - n$ nonbridging oxygens that are only bonded to a potassium cation.

The insert of Fig. 1 highlights the fact that annealing removes the curvature and brings the conductivity in the glass to Arrhenius behavior 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 [15] 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 [Fig. 3(a)] for compositions where no departure from Arrhenius behavior is seen. This is also in agreement with the fact that decrease of density increases conductivity [16] in fast ion conducting glasses. However, we notice also that the temperature at which the non-Arrhenius behavior (NAB) begins (e.g., 635 K or $10^3/T = 1.57$ for the $x = 0.25$ sample) corresponds to a relaxation time of 10^5 s for this kind of glasses, which is several orders of magnitude larger [17] than the experimental time scale of our experiment. The curvature therefore does not appear to be originated by structural relaxation but rather by structure dependent additional processes that we discuss below.

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 (0.7 eV at $T \simeq 400$ K and 0.3 eV at $T \simeq 700$ K). For comparison, the corresponding reported difference [5] for the highest saturated silver superconducting chalcogenide was about 0.15 eV. Therefore, the effect of saturation 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 and 0.93 eV). From the observations made on both figures, it becomes clear that a dramatic change in regime occurs in the composition interval $0.12 < x < 0.17$. This change is also observable from the low-temperature activation energy difference between the annealed and virgin state $\Delta E_A = E_A(\text{annealed}) - E_A(\text{virgin})$ which displays [Fig. 3(a)] a significant drop in the aforementionned compositional interval.

The combination of the point defect model [9] and constraint theory [12] appears to be helpful in understanding the modification of the electrical properties, respectively, with temperature and potassium concentration. The point defect model which emphasizes the analogy with conduction in crystals via defects and may therefore be adapted to describe moderate conductors such as the

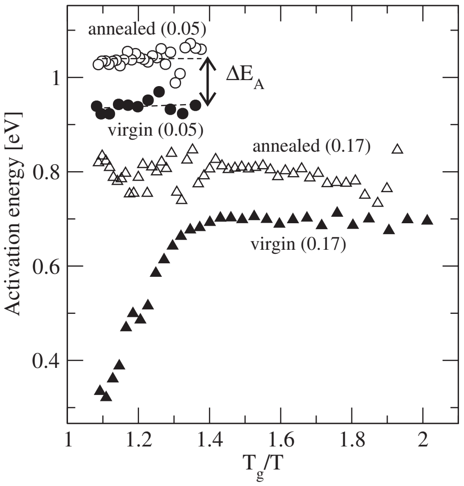

FIG. 2. Running activation energy with respect to T_g/T for the virgin and annealed samples at $x = 0.05$ and $x = 0.17$. Dotted lines correspond to the Arrhenius fit of the data in Fig. 1. ΔE_A [used in Fig. 3(a)] represents the activation energy difference between the annealed and virgin state at low T.

present silicates, suggests that at some temperature in the glass phase the conduction mechanism changes from extrinsic association to extrinsic dissociation diffusion. The former, found at low temperature, corresponds to a regime where not all the defects (vacancies or interstitials) are free to hop whereas the latter does not require defects for the hopping motion of a diffusing ion. In the low-temperature range, one has to overcome an enthalpic barrier ΔH_m for the defect to perform a jump and provide an enthalpy ΔH_a for the association reaction of the defects. At higher temperatures when defects are not necessary for the hopping motion, the barrier reduces to ΔH_m hence reducing the slope in an Arrhenius plot and NAB onsets. For the $x = 0.25$ composition, we find, respectively, 0.65 eV (solid line in Fig. 1) and 0.38 eV (dotted line which is a linear extrapolation of the NAB regime) which provides an estimation for the enthalpy (0.27 eV) for the reorganization (association reaction) of the defects. Alternatively, the local deformation of the network favors hopping motion and permits therefore extrinsic dissociation diffusion.

Lagrange bonding constraint counting (LBCC) that includes bond stretching and bond-bending forces [12] characterizes the compositional threshold. Connections of network rigidity with electrical conduction in solid electrolytes has been established [18] recently. LBCC furthermore correlates quantitatively network modification with the glass-forming tendency in chalcogenide [19] and oxide glasses [20]. The present system can be seen as composed of a network of N atoms among which N_r 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 nonbridging 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 per 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. 3(a). The study of the local structure of potassium silicate glasses obtained from NMR investigation provides a supplementary evidence [28] 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 [Fig. 3(b)]. Furthermore, we notice that a cluster composed of a Q^4 and Q^3 tetrahedron (a "$K_2Si_4O_9$-like" cluster) is optimally constrained (isostatically rigid, satisfying $n_c = 3$) [29] and the corresponding probability of finding the latter is found to be maximum around the same critical concentration of $x_c = 0.14$. Thus at this composition the network is mainly stress-free. For larger concentrations, size increasing cluster approximations (SICA) predict the growing emergence of floppy clusters such as Q^3-Q^3 bondings.

Finally, both LBCC and the point defect model permits to understand the onset of NAB at a given temperature. It has been observed [30] that floppy modes which proliferate at $x > 0.14$ do not have a perfect zero frequency; i.e., in

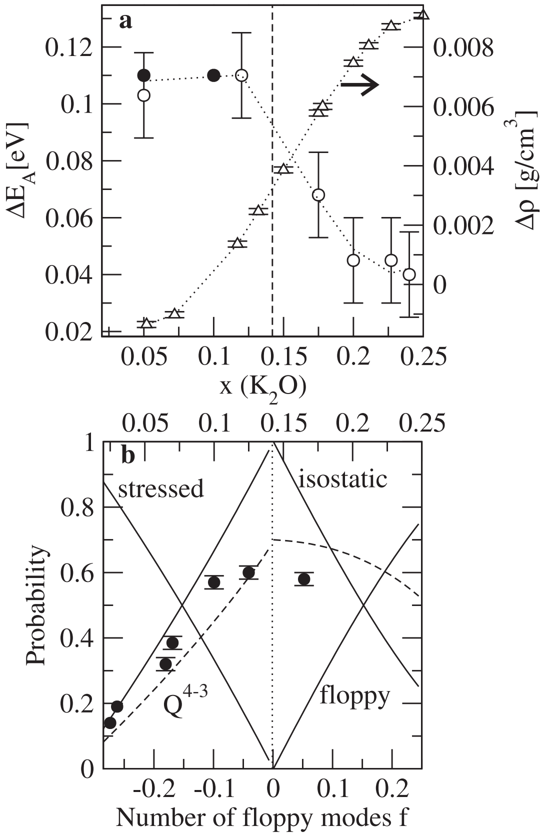

FIG. 3. (a) Low-temperature activation energy difference ΔE_A (open circles) between the virgin and annealed samples, together with previous results obtained (filled circles [27]), as a function of potassium concentration x. Right axis shows the corresponding density change $\Delta\rho$ (open triangles) with annealing. (b) Relative fraction of $Q^{4\text{-}3}$ units (filled circles, from [28]) together with theoretical prediction of the probability of $Q^{4\text{-}3}$ units (broken line) computed from SICA [29]. 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 dotted line corresponds to the mean-field rigidity transition $x_c = 0.14$ where $f = 0$.

real glasses they are shifted by residual forces which are not taken into account in constraint counting algorithms [12] and are important in the case of alkali modified glasses where additional interactions are supposed to take place between cations. This means that in a floppy glass, the deformation of the network requires an energy which is up to about 50 meV that is measured from the low frequency part of the vibrational density of states in analogous silicates [31]. When k_BT becomes of the order of the floppy mode energy, local network deformations can take place to produce defects that can potentially lead to extrinsic dissociation diffusion and saturation effects. For the $x = 0.25$ composition, we measure the onset of NAB at $10^3/T \simeq 1.6$, i.e., $k_BT = 54$ meV which is about the highest floppy mode energy [31]. However, the deformation of the network is only possible when the number of mechanical constraints is lower than the number of degrees of freedom, i.e., when $x > 0.14$.

In summary, we have shown that saturation effects and non-Arrhenius behavior were taking place in the high temperature limit of only certain potassium silicates at compositions where the network is floppy and where the local deformation of the network allows defects. We have pointed out that there was also a clear correlation between the 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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