Supplementary information

Glass structure as a driver of polaronic conductivity in phosphate glasses

containing MoO₃ and WO₃

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1. The MIGRATION concept: the parameters and their implication for the

transport of charge carriers

As described in Section 2.2 in the main text, the model conductivity spectrum and permittivity spectrum is generated for a given set of values of the three model parameters, B, K and $N(\infty)$, mentioned in Eq.1. An experimental conductivity isotherm, as shown in Figure 3(a) in main text is then superimposed on this model spectrum in a log-log representation by shifting it up by the experimental DC conductivity at that temperature along the y-axis and by shifting the experimental isotherm on the scaled frequency axis to ascertain if the chosen value of shape parameter fits the shape of the conductivity dispersion of the experimental isotherm. This procedure is repeated with different model spectrum corresponding to various values of the shape parameter K, until a perfect match is found, see Figure 5(c), and the frequency of onset of conductivity dispersion, v_0 , for each temperature is then determined. The value of parameter K, once found for a given isotherm, is the same for modelling other isotherms for a given glass composition, yielding corresponding values of $v_0(T)$. Normally, B can be chosen arbitrarily large and $N(\infty)$ can be set to zero for this step of determining the correct value of the shape parameter *K*. Experimental permittivity isotherms of Mo-61 and W-66, as well as conductivity isotherms of W-66 corresponding to those modelled in Figure 5 are given below in Figure S1 for completion. The value of the shape parameter *K* is thus crucial for a proper description of the conductivity isotherms of the glass system, since it indicates if the time-dependent decay of the local polarization field induced by the hop of the charge carrier is faster than the reduction in strength of the dipole moment, g(t), itself (1 < K < 2) or is proportional (K = 2) or if there are other obstructing features such as fewer pathways or fewer charge carriers (2 < K < 3). Note that we have for tungsten series, $K \le 2$, whereas for Mo oxide series, K > 2., see Table 3, main text.





For values of the shape parameter $K \ge 2$, deeper insights into what facilitates or hinders the charge carrier hop can be gained in terms of modelling scaled experimental permittivity isotherms. Further, we also found that in this series of binary oxide polaronic glasses, the value of the parameters *B* and $N(\infty)$ can be more precisely fixed by modelling the experimental permittivity spectra in a scaled representation. Scaled representation of permittivity spectra superimposed on the suitable model spectrum for glasses not displayed in main text is shown here in Figure S2 for completion.



Figure S2. Scaled permittivity spectra of (a) W-50, (b) W-61, (c) W-71, (d) Mo-57, (e) Mo-70 and (f) Mo-80 glasses superimposed on corresponding model curves with B = 12.

This helps us calculate the spatial extent of localised diffusion of the charge-carrier [SM1], a material property of the glass, irrespective of whether the charge carrier is an ion or a polaron (cf., Section 3.3.3. and Eq. (3) of the main text). While in the former it is a measure of actual localised spatial diffusion of the ion, in the latter, it can be correlated to the polaron radius [SM2] as defined by Bogomolov and Mirlin [SM3].

Another issue, we wish to discuss in this ESI is that for the current series of binary polaronic glasses we have examined in the main article: a) the change in the shape of conductivity

isotherms as a function of composition; b) the variation of low-frequency permittivity plateau (where available) and c) the correlation of spatial extent of localized transport of the polarons to either DC conductivity or other features of the spectra.

Typically, in ionic glasses with a single conducting species, three patterns of behaviour of these features as a function of glass composition have been observed. We briefly state these patterns here, so as to put in a broader perspective the experimental observation and analysis of conductivity spectra in the current series of binary polaronic glasses described in the main text. Firstly, in the case of binary alkali silicate and borate glasses, there is a monotonic increase in DC conductivity as the concentration of alkali ions is increased, while the shape of spectra remains the same [SM4]. In these systems, the role of the network is mostly to provide more conducting paths despite a steady network modification. The second pattern of behaviour is the one observed in the spectra of binary sodium germanate glasses [SM5] as ion number density is increased. There, the DC conductivity increased monotonically while the shape parameter describing the conductivity spectra decreased monotonically as also the spatial extent of localized diffusion; however, the variations of the scaled permittivity plateau as a function of composition were not monotonical. In particular, the spatial extent of local excursions of ions showed a $x^{-1/3}$ correlation (where x denotes the fraction of sodium oxide) establishing that it is the Coulomb interaction between the sodium ions that plays a dominant role in the ion transport in these glasses and that the role of structure is only marginal.

The third kind of behaviour is exhibited by mixed glass former systems, where the mobile ion concentration is held constant while the relative composition of network forming oxides is varied. In such systems, the DC conductivity as a function of composition displays a maximum at an intermediate composition while there is no change in the shape of the conductivity isotherms. [SM1, SM6] In these systems ionic transport was found to be structure driven, namely, it was the changes in network structure that either facilitated or obstructed ionic

transport, and this was reflected in the correlation of the spatial extent of localized diffusion with the DC conductivity or permittivity respectively.

The above-mentioned patterns, has helped us to interpret our model results carefully and to discover that novel correlations are indeed revealed in the WO₃-P₂O₅ and MoO₃-P₂O₅ glasses in which the amount of WO₃/MoO₃ changes from 49 to 81 mol%. Unlike in the three cases described in the above paragraphs, in these glasses all dynamic values of polaron transport, parameter K, $< r_{loc}^2(\infty) > ^{0.5}$ and $\varepsilon_S(0)$ mirror each other, revealing that the dynamics of polaron transport in these glasses is guided by the interconnectivity of structural units and hence the formation of conduction pathways of the polarons, and has been discussed exhaustively in the main text in Section 3.3.3.

2. EDS analysis

In order to determine the exact glass composition, glass samples were investigated using energy dispersive X-ray analyzer (EDS). Exemplary SEM images and EDS spectra are shown in Figure S3 for Mo-70 and W-71 glasses. As can be seen from the EDS spectra glasses contain small amounts of aluminum and carbon originating from the reaction of the melt with the alumina crucible and graphite mould, respectively. However, since the amounts of these elements are very low, i.e. <0.8 wt% for Al and <3.2 wt% for C at the glass surface but 0 wt% at the cross-section, they are not expected to have any influence on the structure and physical properties of examined glasses.



Figure S3. SEM micrographs of (a) Mo-70 and (b) W-71 glasses and corresponding EDS spectra.

3. ESR analysis

The oxidation states of molybdenum and tungsten ions in the glasses were investigated by electron spin resonance (ESR) spectroscopy. The unreduced Mo⁶⁺ and W⁶⁺ ions are diamagnetic and hence cannot be detected by ESR, while the reduced W⁵⁺ and Mo⁵⁺ ions have spins S=1/2 leading to single resonance line influenced by nuclear hyperfine interactions [SM7, SM8]. The ESR spectra of glasses containing MoO₃, shown in Figure S4(a), exhibit an intense line which arises from the even molybdenum isotopes (*I*=0) with a natural abundance 74.62% and a weak shoulders that correspond to hyperfine structure from odd ⁹⁵Mo and ⁹⁷Mo isotopes with *I*=5/2 and a total abundance 25.68% [SM7, SM8]. Similarly, the tungsten ESR signal, shown in Figure S4(b), exhibits a line associated with tungsten isotopes (*I*=0) and a smaller line that arises from the hyperfine interaction with a single nucleus of the 14.28% abundant ¹⁸³W isotope (*I*=1/2) [SM7, SM8]. With the increase of both MoO₃ and WO₃ the intensity of

ESR signal decreases indicating a decrease in the amount of Mo^{5+} and W^{5+} ions. The M^{5+}/Mo_{tot} and W^{5+}/W_{tot} fraction, determined from the ESR spectra as described in the Section 2.1. Experimental is given in Table 1 in the main text.



Figure S4. ESR spectra of selected glasses from (a) $xMoO_3-(100-x)P_2O_5$ and (b) $xWO_3-(100-x)P_2O_5$, x=49-81 mol%, series.

4. Model-free scaling of conductivity spectra

A detailed analysis of frequency-dependent conductivity in terms of the scaling properties of the spectra allows us to understand various features underlying the charge carrier dynamics. A main approach is to inspect the scaling properties of conductivity spectra in a model-free way. For this purpose, the Summerfield scaling [SM9] is the most widely used procedure due to the easily accessible parameter - σ_{DC} , used as a scaling factor. In this procedure, an attempt is made to superimpose the conductivity curves measured at different temperatures to a single master

curve by plotting $\left(\frac{\sigma(\nu)T}{\sigma_{DC}T}\right)_{VS.} \left(\frac{\nu}{\sigma_{DC}T}\right)_{in a log-log plot. If Summerfield scaling is valid and all conductivity isotherms collapse yielding a conductivity master curve, then the time-temperature superposition principle (TTS) is satisfied. This further signifies that the only role$

of temperature is to speed up (at higher *T*) or slow down (at lower *T*) charge carrier dynamics without changing the conduction mechanism itself.



Figure S5. Conductivity spectra of (a) W-71 and (b) Mo-57 glasses scaled according to the Summerfield procedure.

In this study, Summerfield scaling was successfully applied in most glasses implying that TTS is valid and that the mechanism of polaron conduction in these samples is temperatureindependent. However, three samples, namely Mo-49, Mo-57 and W-81, were found to deviate from the Summerfield scaling. Figure S5(a) shows an example of a successfully constructed conductivity master curve for W-71 glass, whereas Figure S5(b) exhibits a deviation from the Summerfield scaling for Mo-57 glass. Usually, purely polaronic and purely ionic glasses with one type of mobile species obey Summerfield scaling, however, the literature reports several exceptions. Murugavel and Roling [SM10], reported deviations in alkali tellurite glasses and linked their origin to the changes in the number density of mobile alkali ions and/or number of available conduction pathways with temperature. We find it reasonable to infer that in the case of W-81 glass, the non-validity of Summerfield scaling could be related to the traces of crystallization and structural inhomogeneity of the sample due to which polarons are localized in diverse structural environments (crystallized and amorphous) and hence might respond differently to the thermal activation. On the other hand, Mo-49 and Mo-57 glasses are fully amorphous and homogenous, and hence, the structural diversity of different phases cannot be the cause of the failure to construct a conductivity master curve using Summerfield scaling. In these two glasses, however, the non-Summerfield scaling could be related to more subtle structural influences. As detected by Raman spectroscopy, Mo-49 and Mo-57 glasses contain a mixture of MoO₄ tetrahedra and MoO₆ octahedra. Since the Mo-O bonds in these polyhedra were found to be slightly different in length (1.8 Å in MoO₄ and 2.0 Å in MoO₆ [SM11]), it seems likely that both types of polyhedra participate in the polaron transport but due to different length and energy of the Mo-O bonds, the polaron transport through them is differently thermally activated. In line with this, it is interesting to note that for other molybdenum glasses with dominant MoO₄ tetrahedra, and in all WO₃-P₂O₅ glasses containing solely WO₆ octahedra, Summerfield scaling was successful.

In order to inspect the validity of TTS in Mo-49 and Mo-57 glasses it is useful to consider the Sidebottom scaling procedure [SM12] that accounts both changes in the number density as well as changes in the typical hopping distance of the mobile species, and is a more general form of TTS principle, see discussion in Ref. SM2. This type of scaling is obtained by plotting

$$\left(\frac{\sigma(\omega)T}{\sigma_{DC}T}\right)_{\text{versus}} \left(\frac{\varepsilon_0 \Delta \epsilon}{\sigma_{DC}}\omega\right)_{\text{in which }} \Delta \varepsilon = \varepsilon(0) - \varepsilon(\infty) \text{ is called the dielectric strength and is}$$

given by the difference in low-frequency permittivity plateau and the high-frequency permittivity caused by vibration and electronic polarization. As can be seen in Figure S6, the Sidebottom procedure yields a super-master curve for Mo-49 and Mo-57 glasses confirming the TTS principle and unchanged polaronic conduction mechanism in these glasses. Here, it should be noted that since the low-frequency permittivity plateau $\Delta\epsilon$ could not be reliably estimated from the experimental permittivity spectra for Mo-49, $\Delta\epsilon$ was estimated using

relation $\Delta \varepsilon = \frac{\sigma_{DC}}{\varepsilon_0 f_0}$ where f_0 denotes the onset frequency of conductivity dispersion read

off at $\sigma'(f_0) = 2 \cdot \sigma_{DC}$; as in refs [SM13, SM14]. This method of estimation has also been applied for the Mo-57 glass in Figure S6, despite it having an experimentally well estimated $\Delta \varepsilon$ and obeying Sidebottom scaling, to demonstrate the soundness of this procedure.



Figure S6. Conductivity spectra of (a) Mo-49 and (b) Mo-57 glasses scaled according to the Sidebottom procedure.

In summary, we can state that the model-free scaling of the conductivity spectra in all systems (except of partially crystallized W-81 glass) confirmed temperature independent mechanism of conduction. However, by utilizing Summerfield scaling procedure we could obtain a finer insight into the thermal behavior of polarons associated with different structural units in the glass network i.e. molybdate tetrahedra and octahedral.

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