Spectral analysis

The *extended log-normal* function used to analyse the Raman spectra (*eLN*) is the sum of a log-normal function accounting for the boson peak and an increasing exponential reproducing the continuum of vibrational modes captured in a Raman experiment up to the cutoff frequency around 500 cm^{-1}.

$$I_{eLN}(\omega) = A_1 \exp\left\{-\frac{1}{\Gamma}\left[\log\left(\frac{\omega}{\omega_0}\right)\right]^2\right\} + A_2\,\omega \exp\left\{\alpha\omega\right\} \quad (1)$$

A_1 and A_2 are the amplitudes, ω_0 is the maximum of the log-normal function, γ is a width factor, and α is the slope of the exponential. Eq. 1 is able to produce a large variety of spectral shapes above the boson peak maximum, including fast decreases to zero (purely lognormal) or high level and flat backgrounds (Fig. 1). In order to account for the fast decay around 500 cm^{-1} in almost all spectra, we added a gaussian decay beyond a cutoff frequency ω_c. Thus, the fit can be performed in the entire frequency range between $\sim$ 20 cm^{-1} and $\sim$ 600 cm^{-1} (*i.e.* after the cutoff frequency) without defining manually anchor points, or an upper frequency limit arbitrarily setting the background level. Moreover, the parameters evolve very smoothly with composition within a glass family, and it was also possible to reproduce the diversity of background shapes between different glass families. Fitting examples are

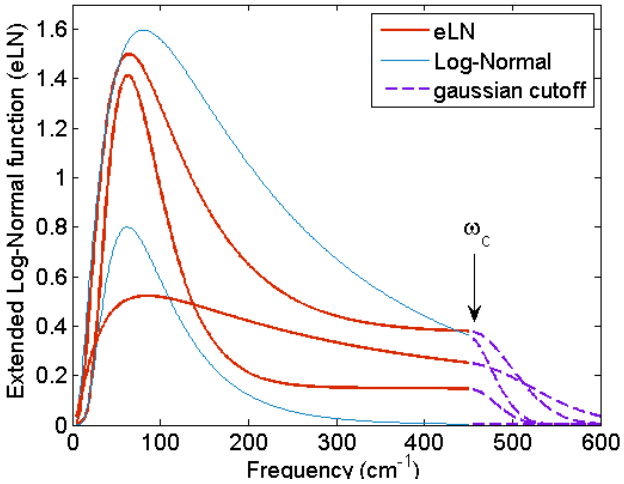

Figure 1: Examples of spectral shapes of the eLN function, from purely log-normal (thin lines, $A_2 = 0$) to highly extended-type (thick lines, $A_2 \neq 0$), with a gaussian cutoff decay at ω_c (dashed lines).

given in Fig. 2a for BAS glasses. The cation modes ω_1 and ω_2 are reproduced by gaussian functions and fitted simultaneously with Eq. 1. In that glass familly, a weak additional gaussian was added to account for a structured feature which indeed appears around 430 cm^{-1}, slightly before the cutoff frequency.

Other fitting functions have been tested in order to confirm the validity of the results for ω_1 and ω_2, as for example the *asymmetric log-normal* spectral form (aLN) [1]:

$$I_{aLN}(\omega) = A \exp\left\{-\log(2)\left[\frac{\log(1+2a\frac{\omega-\omega_{BP}}{\gamma})}{a}\right]^2\right\} + I_0 \quad (2)$$

A is the amplitude, ω_{BP} is the boson peak frequency, γ is the width of the log-normal function, a is

the asymmetry parameter, and I_0 is an offset. In that case, we deliberately fixed the upper limit of the fitting domain near ω_2. This raises the background level to its highest value and provides a situation significantly different to the previous one (Fig. 2b). This operator-defined frequency limit adds to the

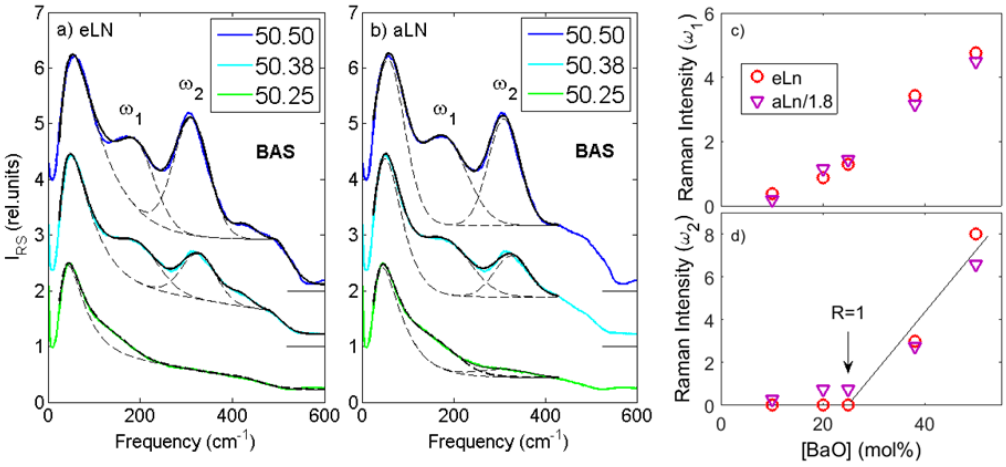

Figure 2: **a)** BAS glasses fitted with the eLN function followed by a gaussian cutoff in BAS. **b)** BAS glasses fitted with aLN function with an operator-defined upper frequency limit (430 cm^{-1}). For sake of clarity, the spectra have been translated verticaly as indicated by the horizontal lines on the right. **c)** and **d)**, Integrated intensity of ω_1 and ω_2, respectively, obtained in BAS glasses using the two fitting procedures. In panel c) the values obtained by a fit with aLn have been devided by 1.8.

five fitting parameters of Eq. 2 and leads therefore to the same number of free parameters as for the first method.

As a first result we find that the peak position of ω_1 and ω_2 is quite robust and does not depend on the fitting procedure. The integrated intensities however, which correspond to the amplitude of the response times its width, are likely to be more sensitive since they are background-level dependent. The latter are shown in Figures 2c and 2d for modes ω_1 and ω_2 respectively, for the BAS glasses. Depending on the fitting strategy, the values may be different (in particular for ω_1) but the trends are very similar supporting therefore the relevance of the spectral analysis: I_{ω_1} becomes zero when z=[BaO] tends to zero, while I_{ω_2} exhibits a much faster decrease and reaches zero close to the peralkaline to peraluminate join, $R = 1$. Fits using aLN might however indicate that a broad and weak contibution of ω_2 remains in the paraluminate domain ([BaO] $\leq$ 25). If confirmed, this could arise from ill-defined cation motions of ω_2-type close to $(AlO_4)^-$ tetrahedra.

References

[1] M.F. Ando, O. Benzine, Z. Pan, J.-L. Graden, K. Wondraczek, S. Grimm, K. Schuster, and L. Wondraczek, Boson peak, heterogeneity and intermediate-range order in binary SiO_2-Al_2O_3 glasses, Scientific Reports, **8**, 5394 (2018).