Proton jump diffusion dynamics in hydrated barium zirconates studied by high-resolution neutron backscattering spectroscopy (supporting information)

Daria Noferini,[†,‡] Bernhard Frick,[‡] Michael Marek Koza,[‡] and Maths Karlsson[*,†]

[†]Department of Chemistry and Chemical Engineering, Chalmers University of Technology, SE-412 96 Göteborg, Sweden

[‡]Institut Laue-Langevin, CS 20156, 38042 Grenoble Cedex 9, France

1 Fits of the dynamic structure factor

Fig. S1 displays examples, for all the samples, of the fits of the $S(Q,\hbar\omega,T)/S'(Q,0,2\text{ K})$ spectra with a sum of a Lorentzian function and a delta function having Q-independent intensities, and a flat Q-dependent background. Data and fits are shown for T= 550 K, and Q = 0.82 and 1.18 Å^{-1}.

2 Jump-diffusion models

The Chudley-Elliot[S3], Singwi-Sjölander[S4], and Hall-Ross[S5] models (CEM, SSM, HRM, respectively) all assume a diffusive motion *via* successive jumps with a mean residence time τ between two jumps, however, are differentiated by their jump lengths and (Lorentzian) broadenings. In the CEM, the jump distance l_{CEM} is a constant and the (Lorentzian) broadening is given by

$$\frac{\Gamma}{2} = \frac{\hbar}{\tau}\left(1 - \frac{\sin(Ql_{\text{CEM}})}{Ql_{\text{CEM}}}\right), \tag{1}$$

In the SSM, the jump distance $\rho(r)$ is exponentially distributed,

$$\rho(r) = \frac{r}{r_0^2}\exp\left(-\frac{r}{r_0}\right), \tag{2}$$

and the broadening is given by

$$\frac{\Gamma}{2} = \frac{\hbar}{6\tau}\frac{Q^2 l_{\text{SSM}}^2}{1+\frac{Q^2 l_{\text{SSM}}^2}{6}}, \tag{3}$$

where l_{SSM}^2 is the mean square jump length, which is equal to $\int_0^\infty r^2\rho(r)dr = 6r_0^2$.

And in the HRM, the jump distance is defined by a Gaussian distribution,

$$\rho(r) = \frac{2r^2}{r_0^3(2\pi)^{1/2}\exp\left(-\frac{r^2}{2r_0^2}\right)}, \tag{4}$$

and the broadening is given by

$$\frac{\Gamma}{2} = \frac{\hbar}{\tau}\left[1-\exp\left(-\frac{Q^2 l_{\text{HRM}}^2}{6}\right)\right]. \tag{5}$$

The mean square jump length for this model, l_{HRM}^2, is equal to $\int_0^\infty r^2\rho(r)dr = 3r_0^2$.

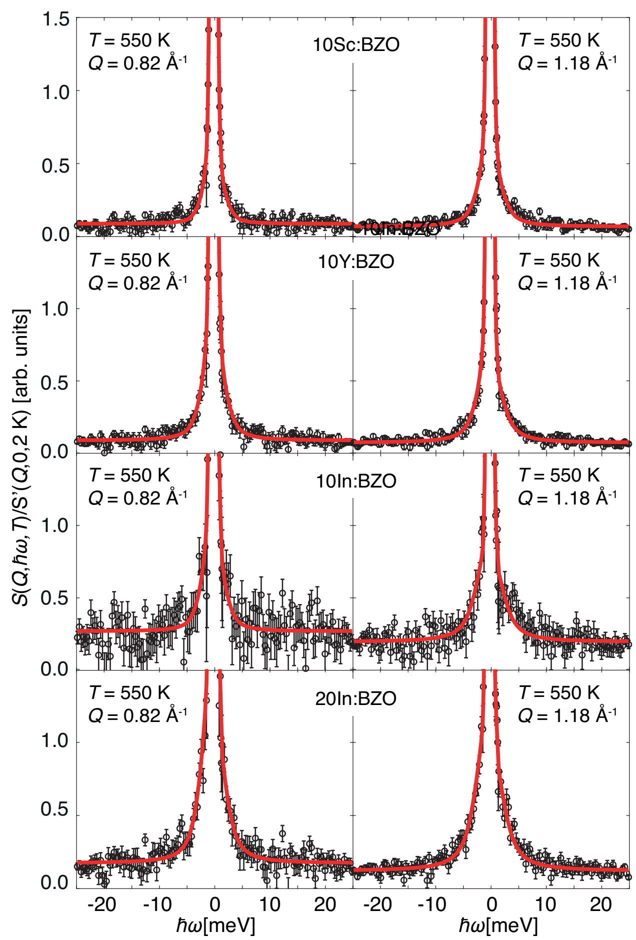

Fig. S1 Data (bullets) and fits (red lines) with a sum of a Lorentzian function and a delta function having Q-independent intensities, and a flat, Q-dependent, background.

2.1 Residence times and diffusion coefficients

The residence times obtained by fitting the quasielastic broadening, Γ, using the CEM, the SSM and the HRM, respectively, are given in Tab. S1. The residence times were used together with the jump lengths given in Tab. S1 to calculate the diffusion coefficients, D, according to the relation $D = \frac{l^2}{6\tau}$. The so-obtained values are listed in Tab. S2.

	CEM			SSM			HRM		
	350 K	450 K	550 K	350 K	450 K	550 K	350 K	450 K	550 K
10Sc:BZO	-	-	0.65(8)	-	-	0.4(2)	-	-	0.5(1)
10Y:BZO	-	-	0.53(6)	-	-	0.4(1)	-	-	0.46(7)
10In:BZO	0.9(2)	0.6(1)	0.53(8)	0.5(2)	0.4(1)	0.3(1)	0.7(2)	0.5(1)	0.42(9)
20In:BZO	1.4(5)	0.9(1)	0.50(3)	1.0(4)	0.6(1)	0.33(4)	1.2(4)	0.8(1)	0.40(3)

Tab. S1 Residence times τ (in ns) obtained by the fit of the quasielastic broadening according to Eq. (1), (3), and (5).

	CEM			SSM			HRM		
	350 K	450 K	550 K	350 K	450 K	550 K	350 K	450 K	550 K
10Sc:BZO	-	-	3(1)	-	-	4(5)	-	-	3(2)
10Y:BZO	-	-	3(1)	-	-	8(8)	-	-	5(3)
10In:BZO	1.8(6)	2.6(8)	2.9(8)	2.4(2)	3.6(3)	3.9(3)	2(1)	3(1)	3(1)
20In:BZO	1.0(4)	1.5(2)	2.8(3)	1.5(7)	2.3(8)	4(1)	1.1(5)	1.8(3)	3.3(6)

Tab. S2 Diffusion coefficients (in $Å^2$/ns), obtained from the fitting with the CEM, the SSM and the HRM, respectively.

References

S1 D. Noferini, M. M. Koza, P. Fouquet, G. J. Nilsen, M C. Kemei, S. M. H. Rahman, M. Maccarini, S. Eriksson and M. Karlsson *J. Phys. Chem. C*, **120**, (2016) 13963–13969.

S2 D. Noferini, M. M. Koza, S. M. H. Rahman, Z. Evenson, G. J. Nilsen, S. Eriksson, A. R. Wildes and M. Karlsson *Phys. Chem. Chem. Phys.*, (2018), DOI: 10.1039/c7cp07340b.

S3 C. T. Chudley, R. J. Elliott, *Proc. Phys. Soc.* **77** (1961) 353–361.

S4 K. S. Singwi, A. Sjölander, *Phys. Rev.* **119** (1960) 863–871.

S5 P. L. Hall, D. K. Ross, *Mol. Phys.* **42** (1981) 673–682.