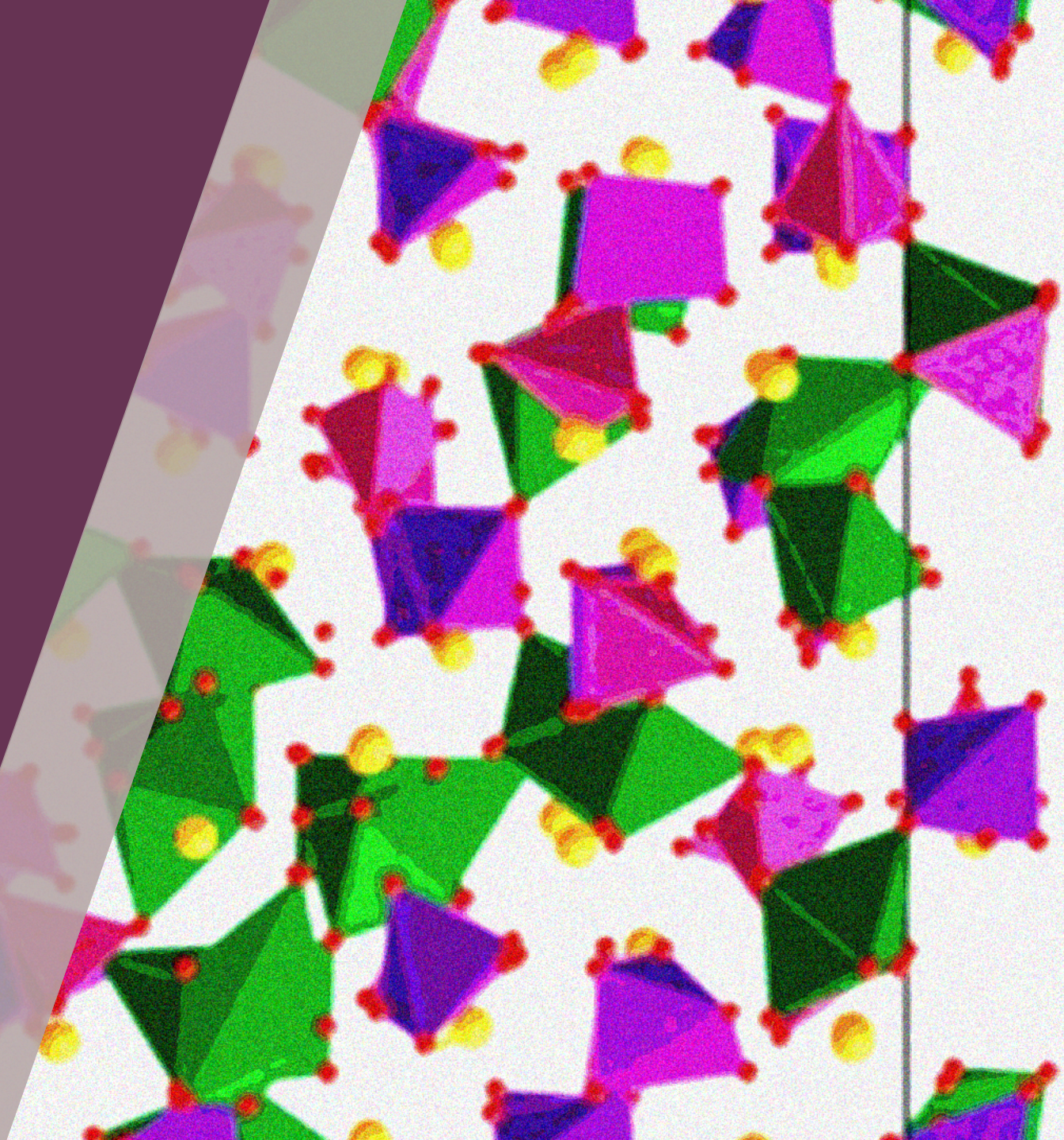
A combined **computational and experimental** approach to studying complex **oxide ion conductors**

Chloe Fuller

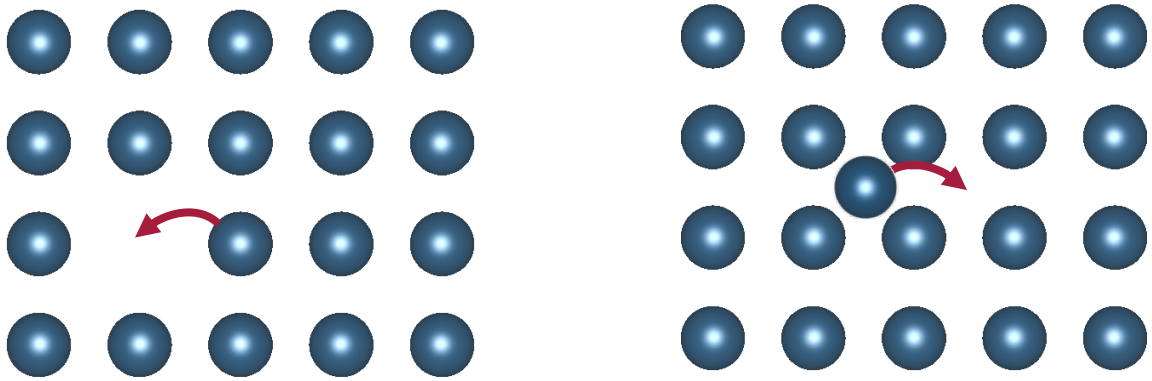
Durham University



Acknowledgements

- Joseph R. Peet (Durham & ILL)
- Bernhard Frick (ILL)
- Michael M. Koza (ILL)
- Mark R. Johnson (ILL)
- Andrea Piovano (ILL)
- Ivana Radosavljevic Evans (Durham)

Solid Oxide Ion Conductors



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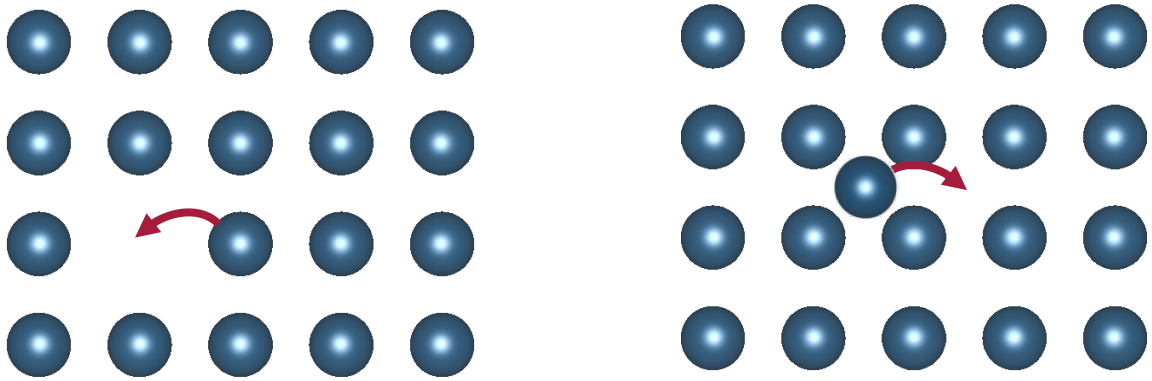
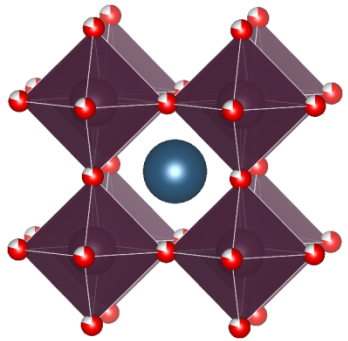


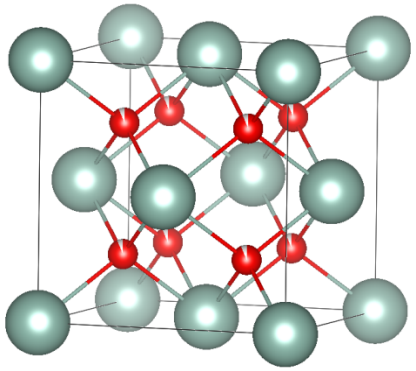
Perovskites

$La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-\delta}$



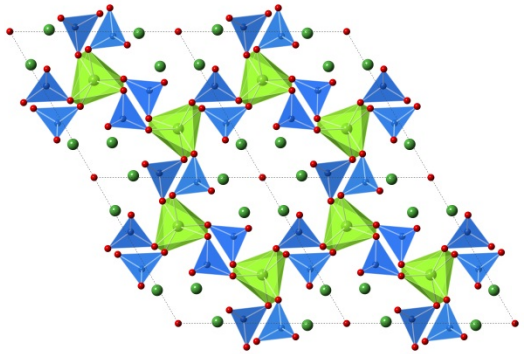
Fluorite-type

$Zr_{1-x}Y_xO_{2-x/2}$



Apatite-type

$La_{9.33+x}Ge_6O_{26+1.5x}$



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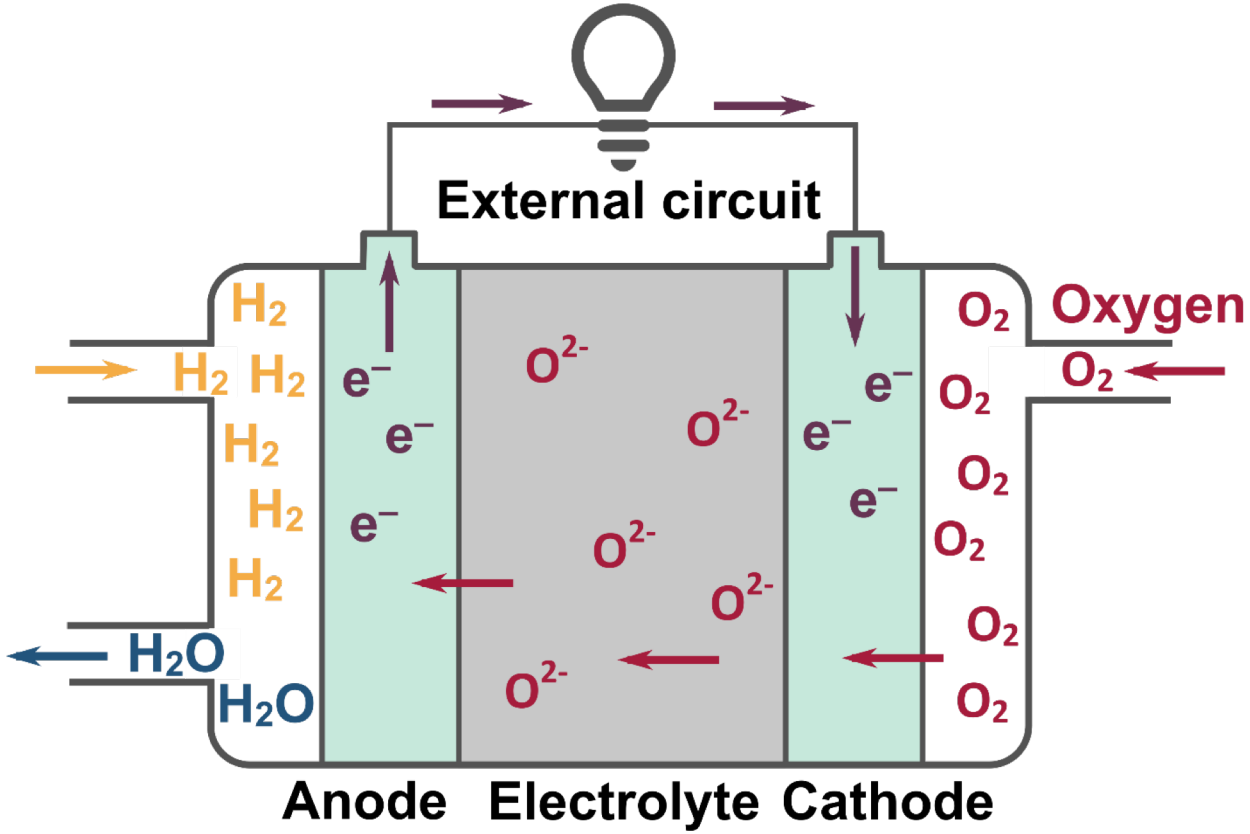
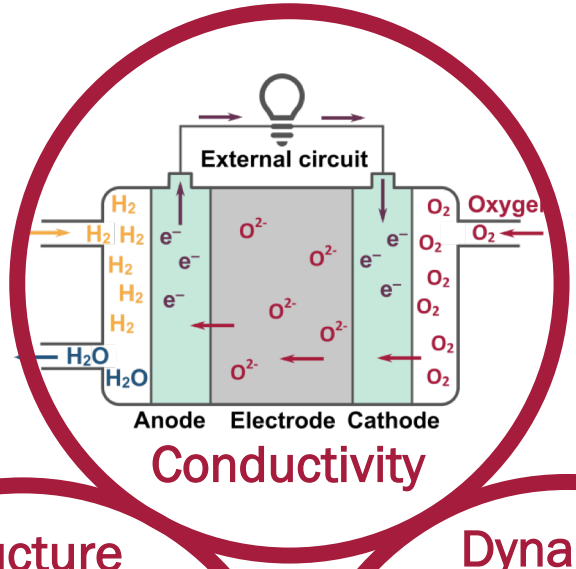


$H_2 + O^{2-} \rightarrow 2e^- + H_2O$

$0.5O_2 + 2e^- \rightarrow O^{2-}$

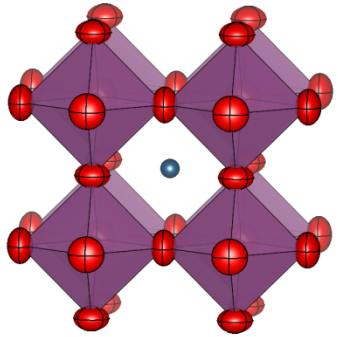
Structure-Property Relationships



Conductivity

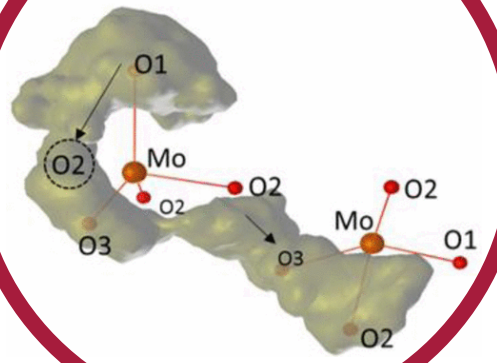
- Impedance spectroscopy
- Tracer diffusion

Structure



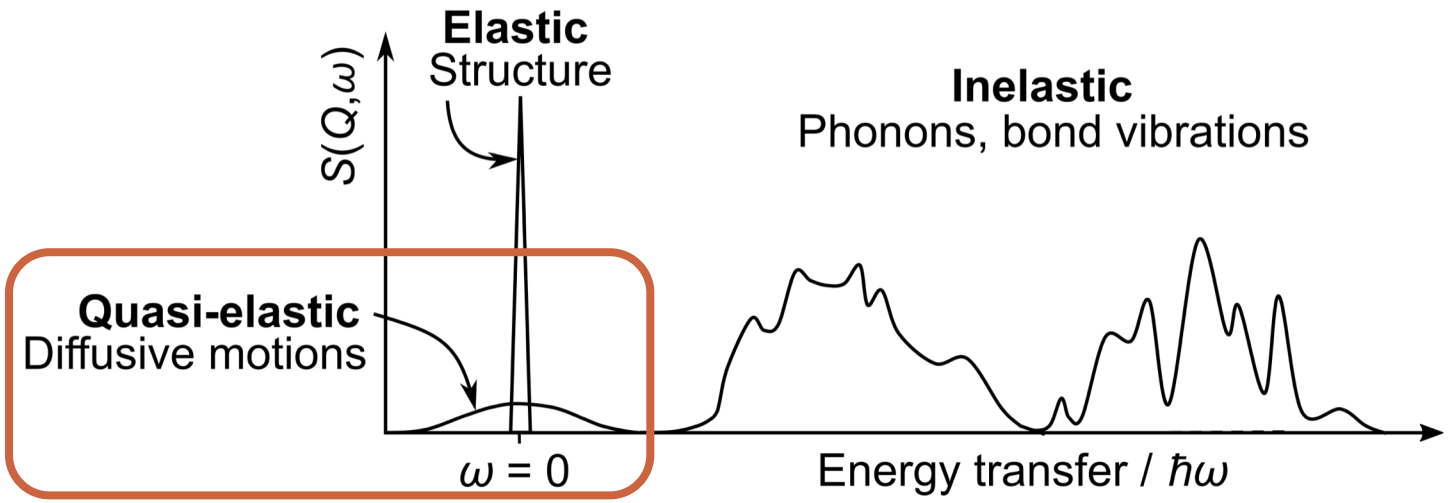
- Diffraction
- Total scattering
- NMR

Dynamics



- QENS
- NMR
- Computer modelling

Methods – Quasi-elastic Neutron Scattering



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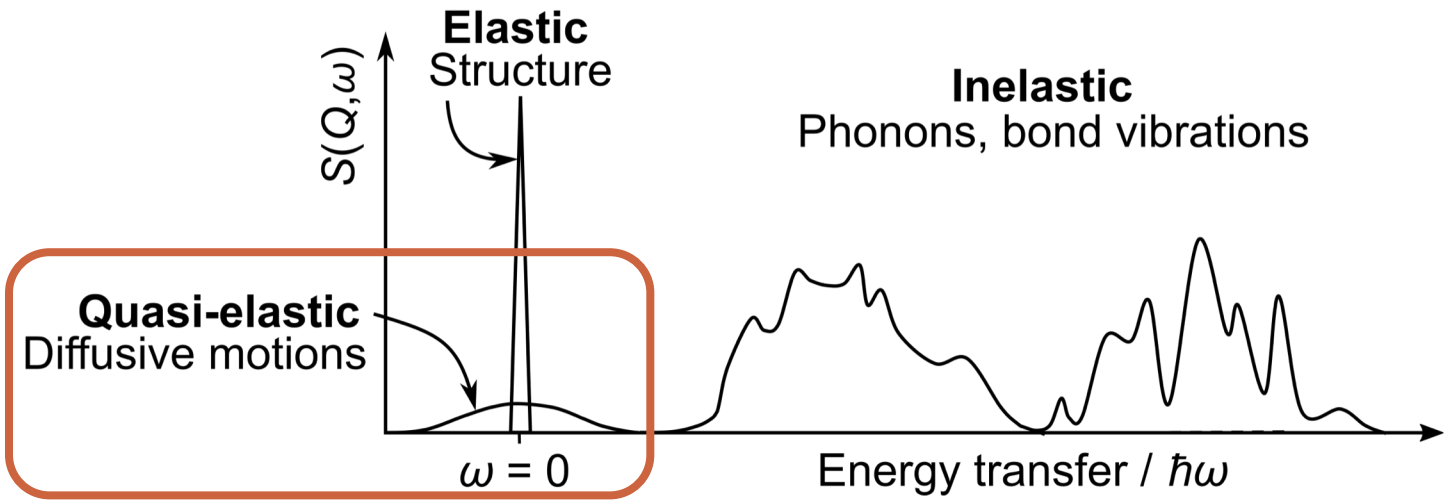
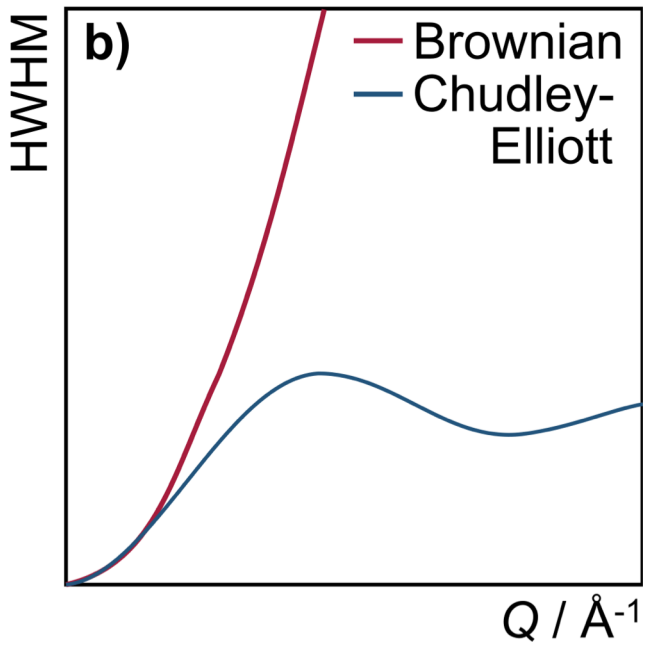
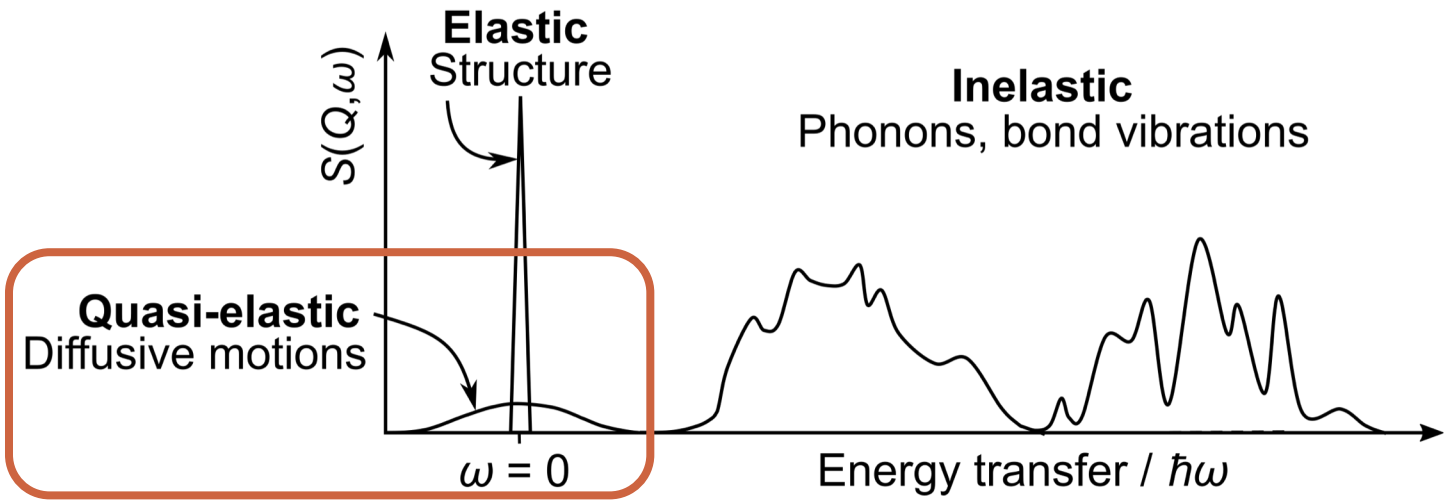


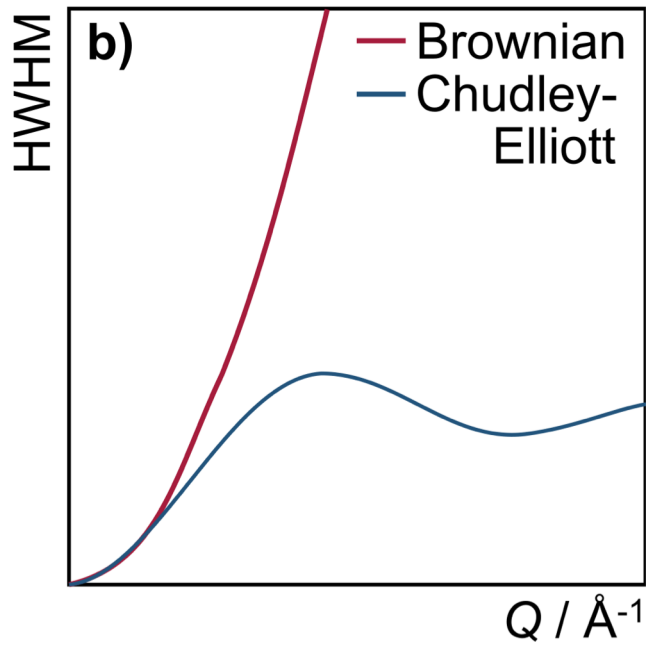


$$\Gamma = \frac{1}{\tau}\frac{(1-\sin(Ql))}{Ql}$$

Methods – Quasi-elastic Neutron Scattering



	b_{coh}	b_{incoh}
O	5.8	0
H	-3.74	25.3



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Methods – *ab initio* Molecular Dynamics

- Predictive
- Atomic-level detail
- Comparable time/length scale to QENS

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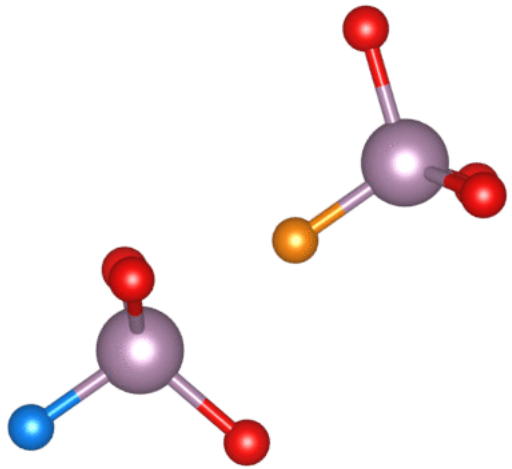

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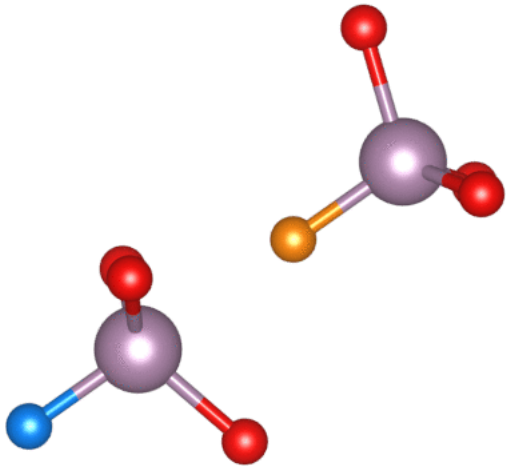
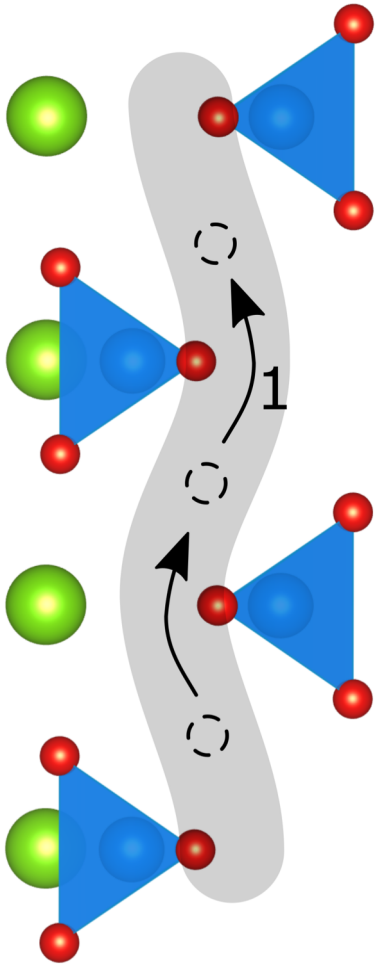
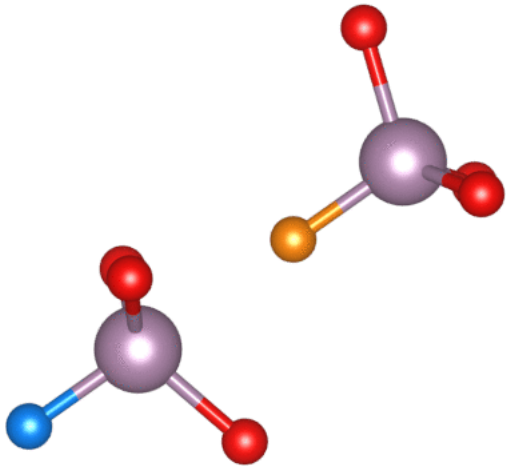


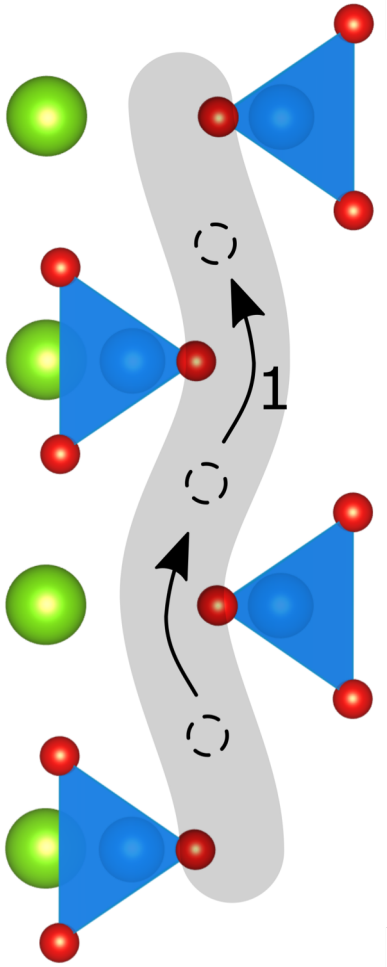


Methods – *ab initio* Molecular Dynamics

- Predictive
- Atomic-level detail
- Comparable time/length scale to QENS

- Theory is hard
- Computationally expensive
- Qualitative





$Bi_{0.913}V_{0.087}O_{1.587}$

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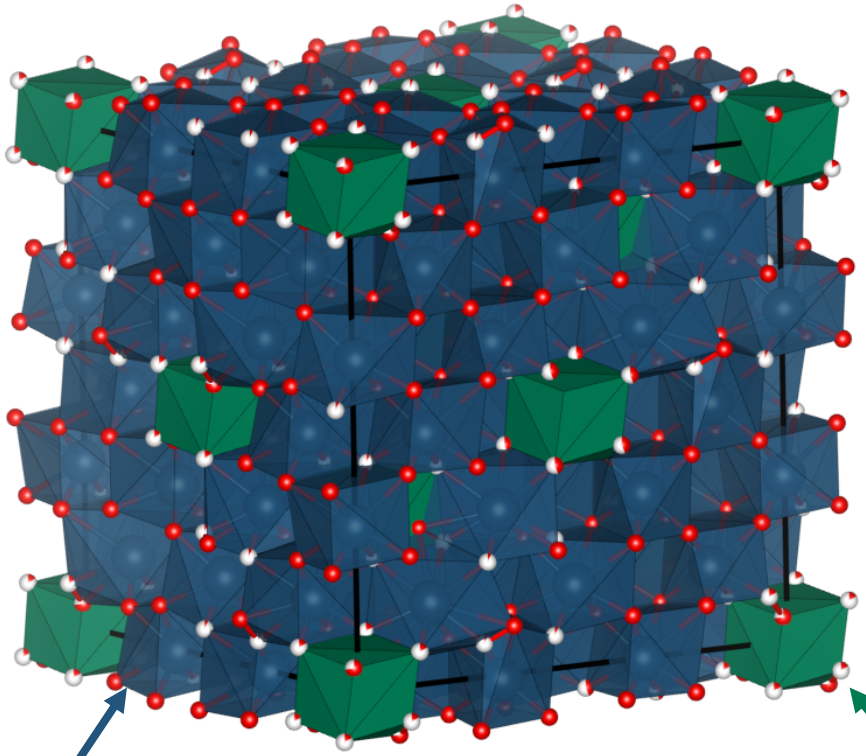
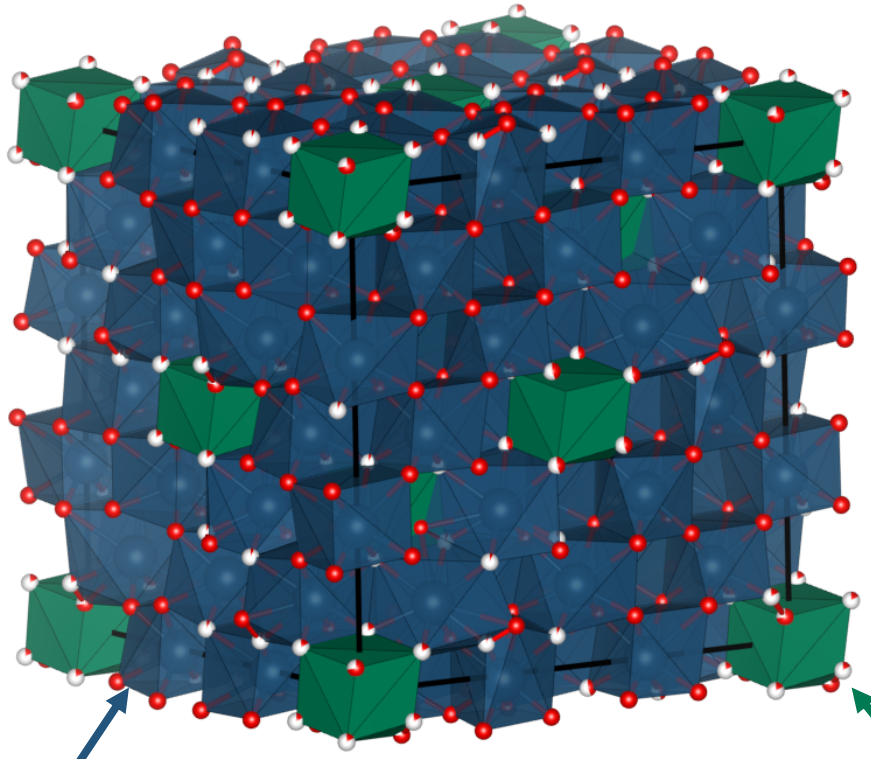


Bi-O sublattice

V-O sublattice

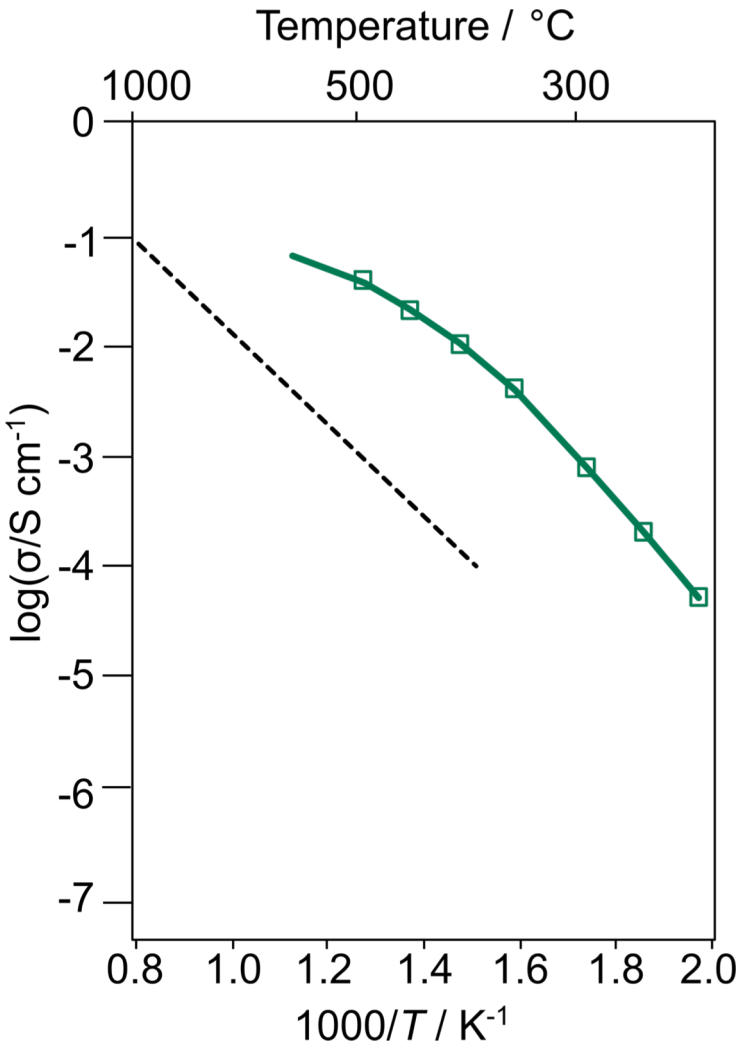
$Bi_{0.913}V_{0.087}O_{1.587}$



Bi-O sublattice

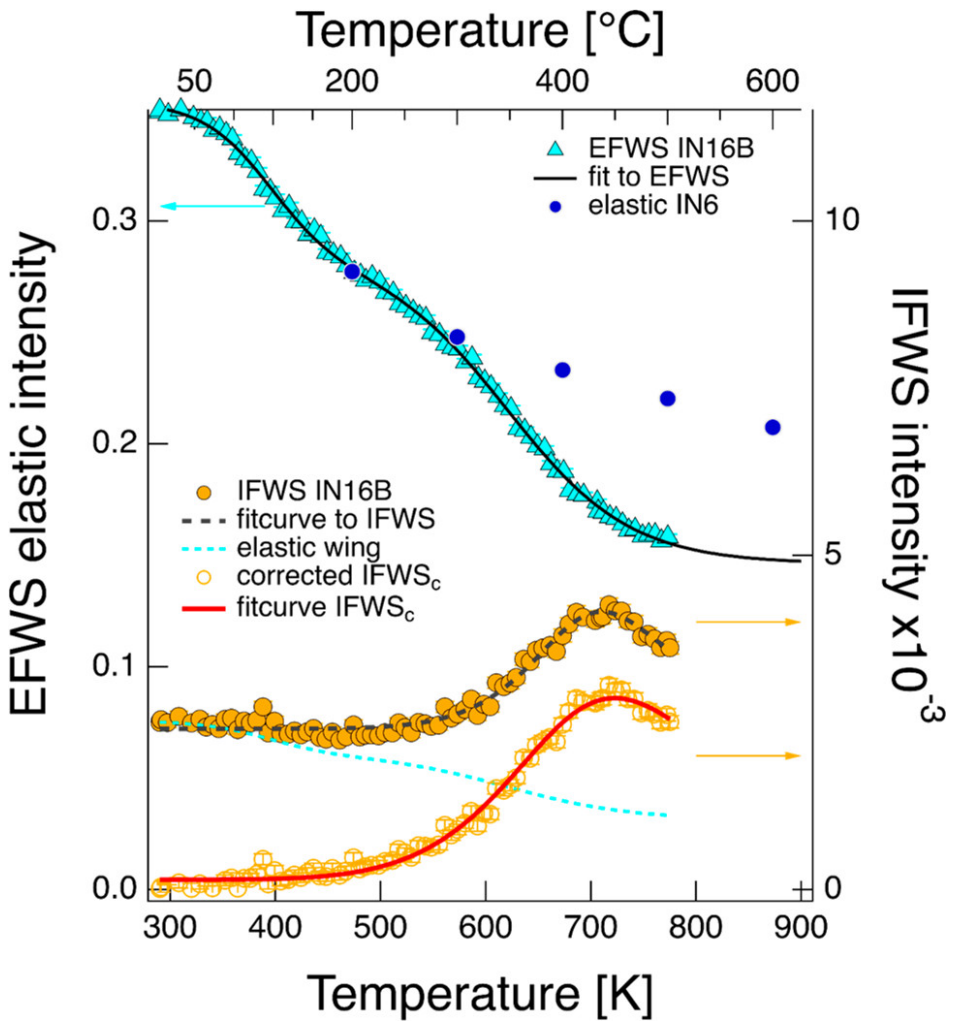
V-O sublattice

3.9×10^{-2} S cm^{-1} at 500 °C



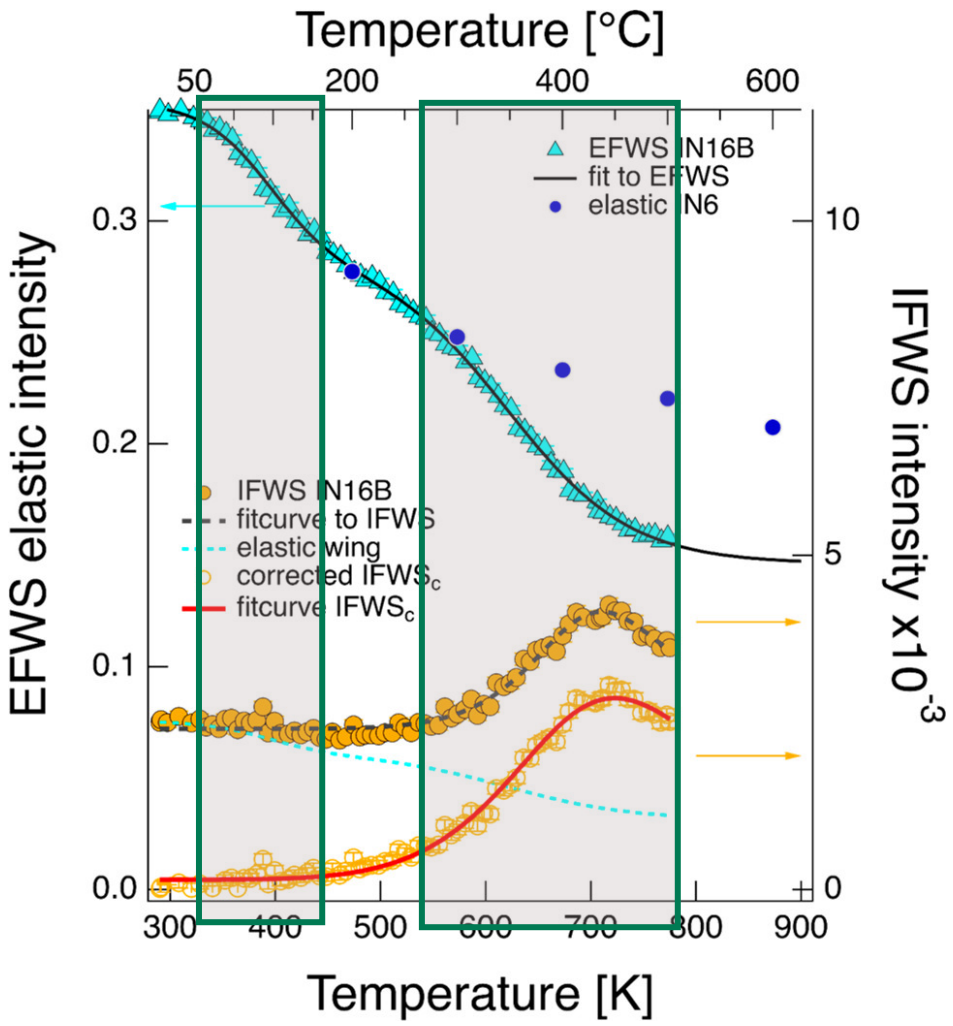
Angew. Chem., Int. Ed. **2012**, *51*, 690

$Bi_{0.913}V_{0.087}O_{1.587}$: QENS



J. Am. Chem. Soc. 2019, 141, 25, 9989–9997

$Bi_{0.913}V_{0.087}O_{1.587}$: QENS



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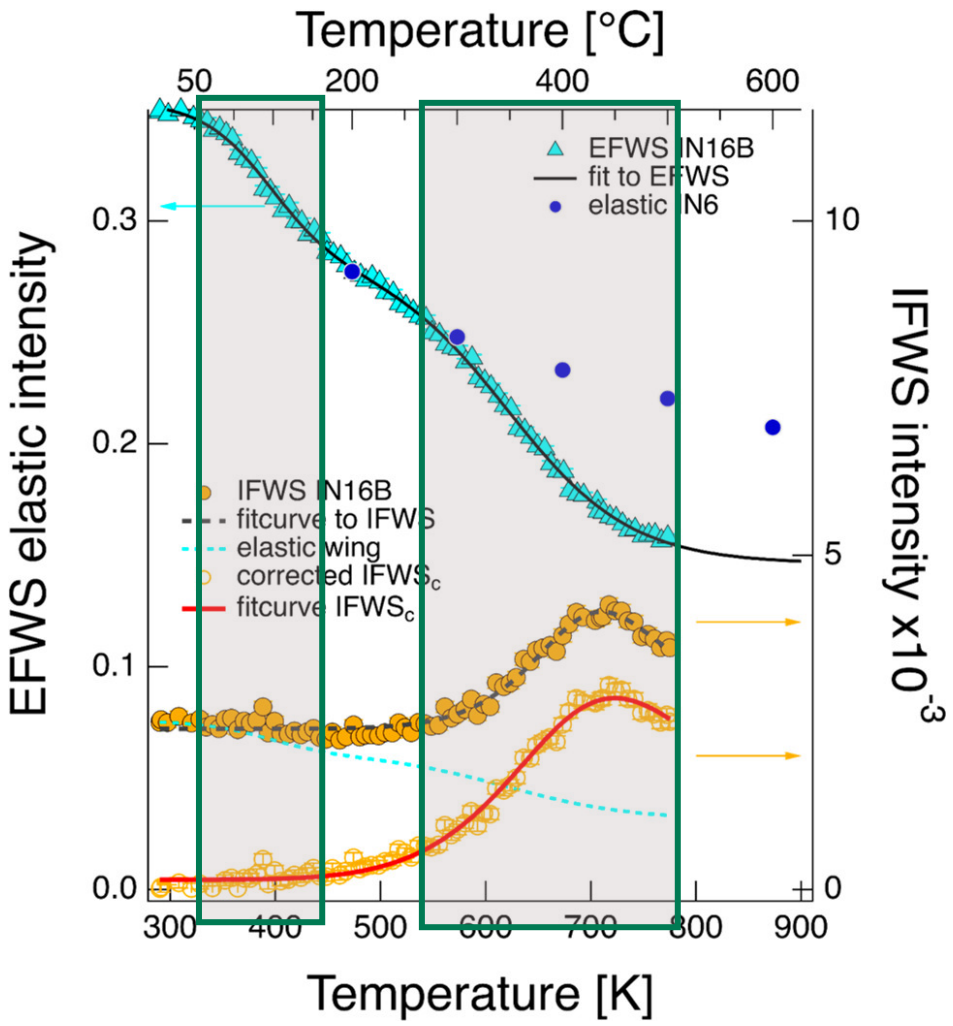

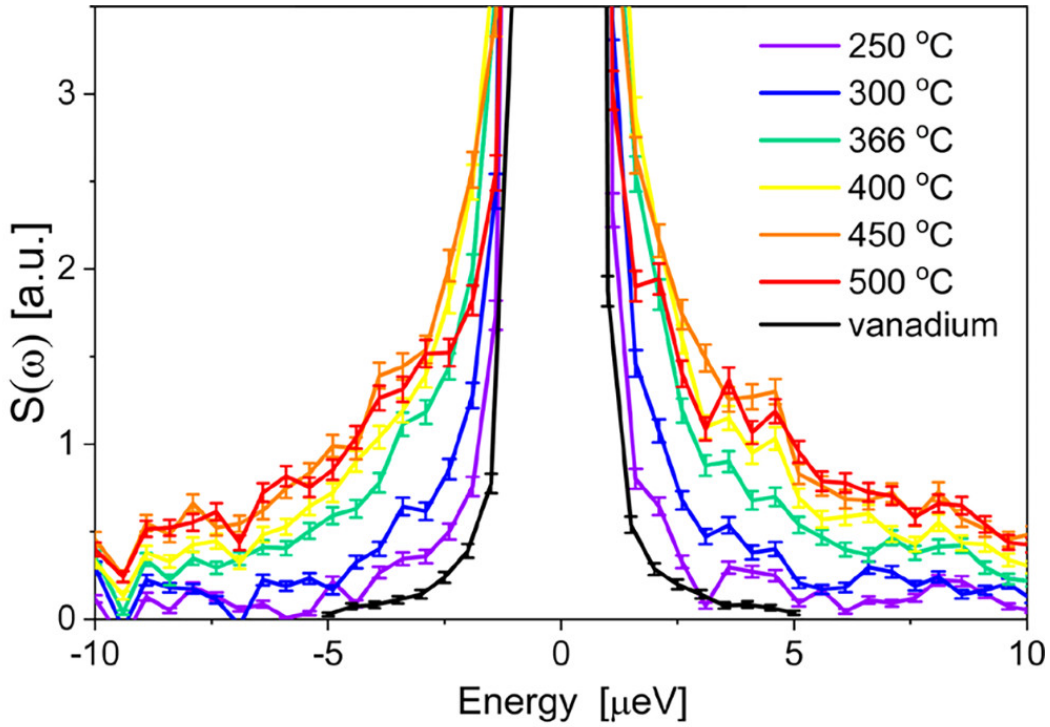

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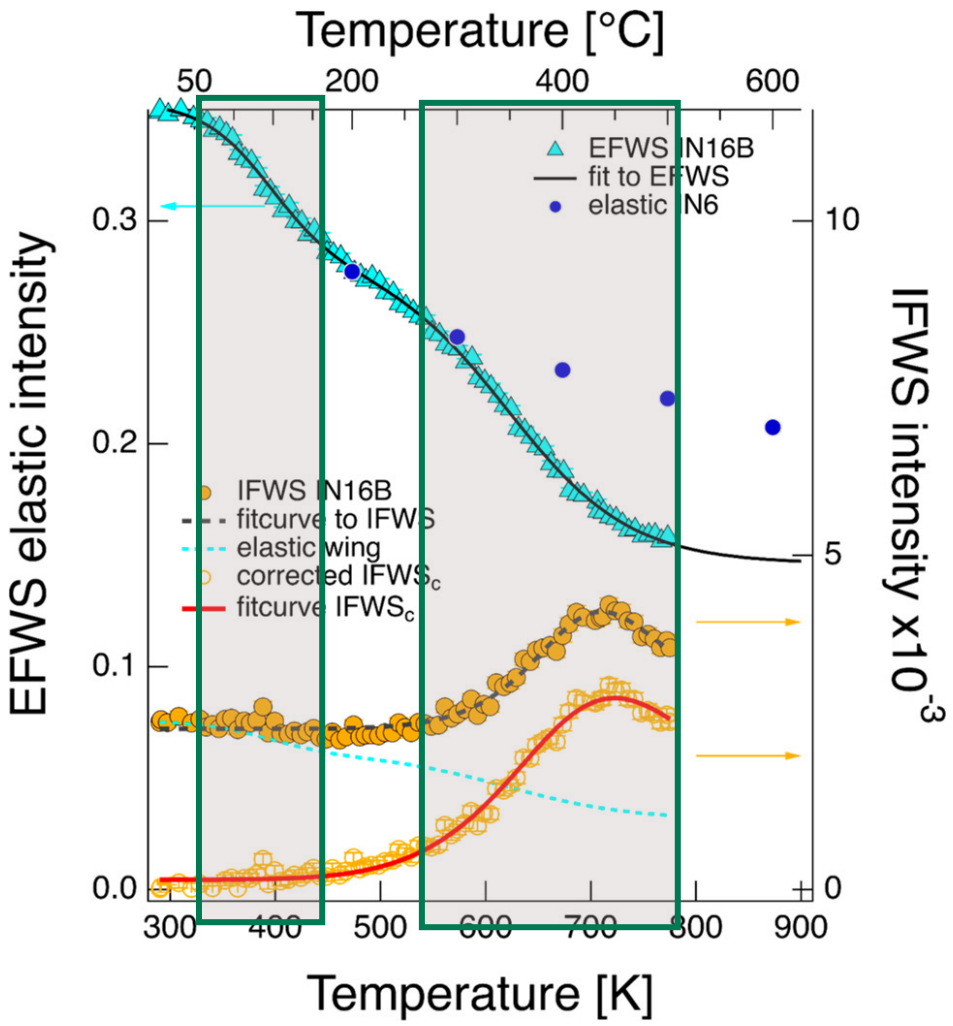
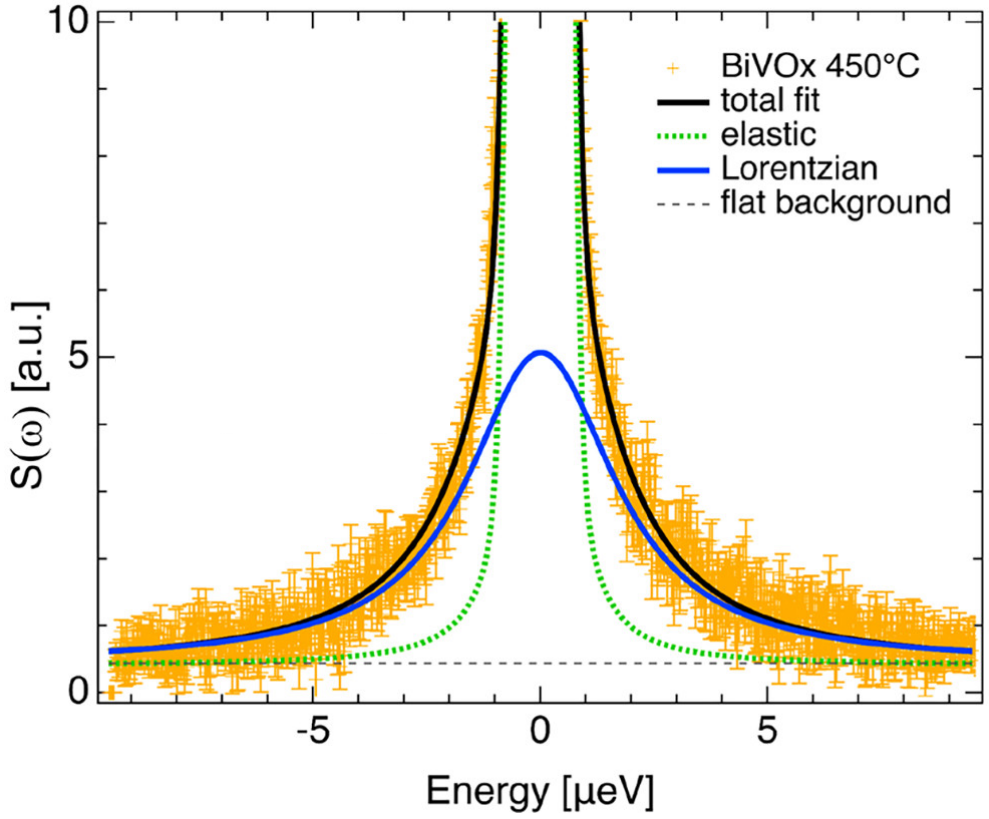


QENS signal fitting



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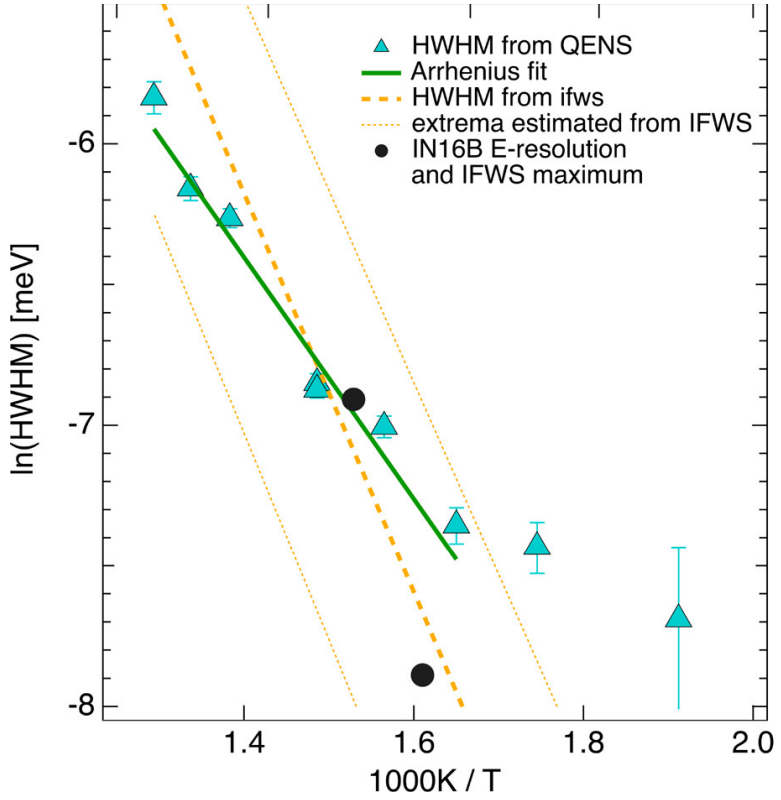
$Bi_{0.913}V_{0.087}O_{1.587}$: QENS

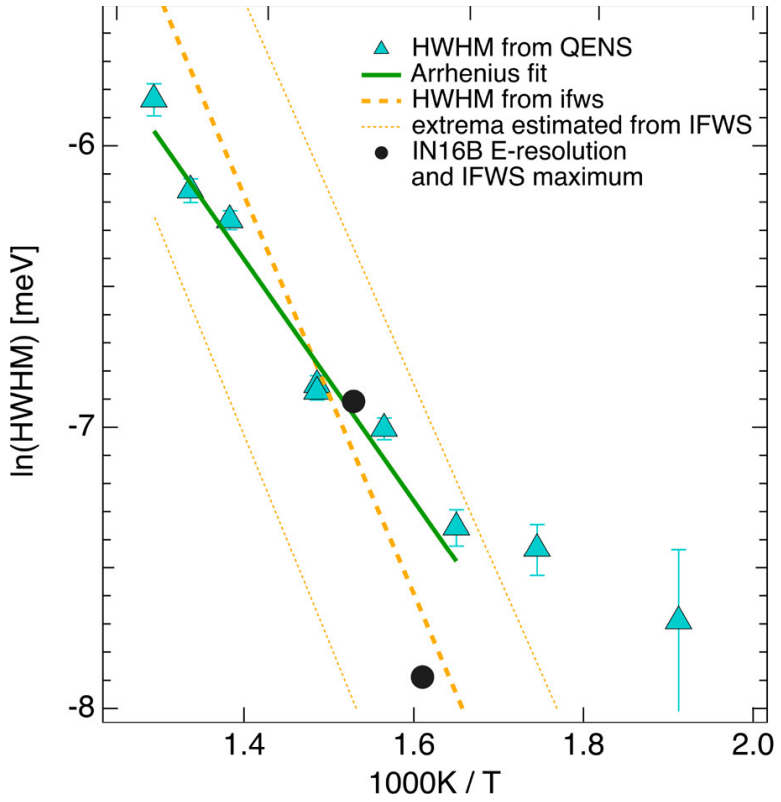
T-dependence of Γ



E_a = 0.39(4) eV

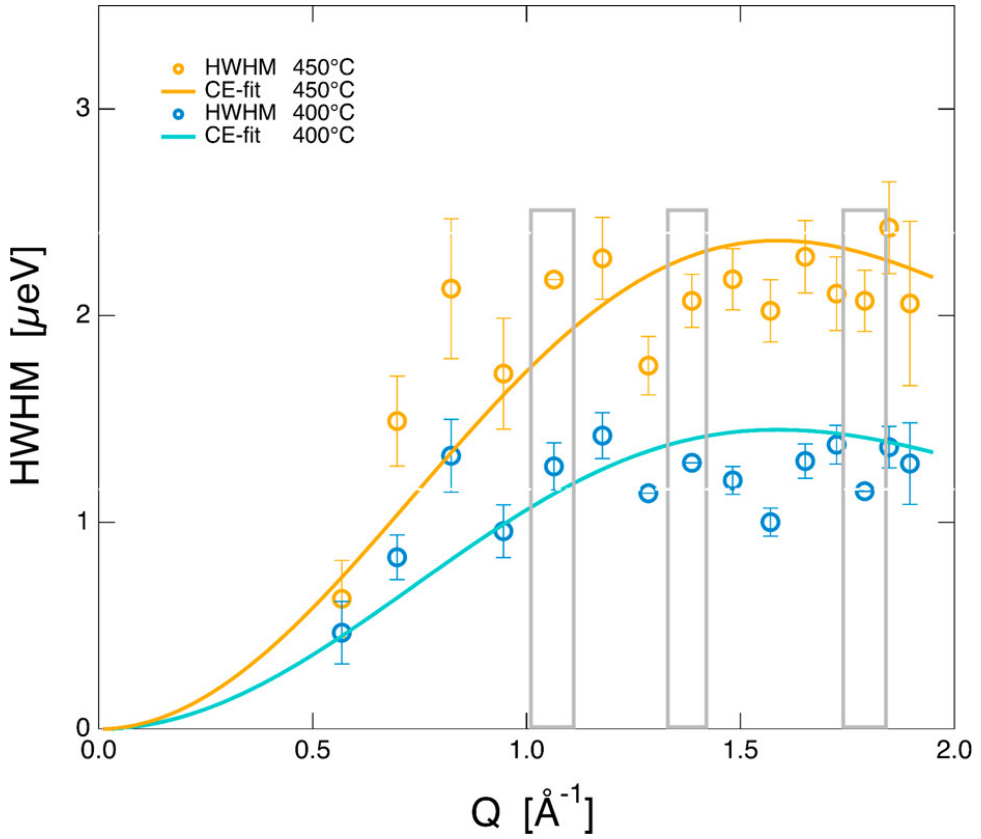
$Bi_{0.913}V_{0.087}O_{1.587}$: QENS

T-dependence of Γ



E_a = 0.39(4) eV

Q-dependence of Γ



l = 2.83 Å τ = 1 ns

$Bi_{0.913}V_{0.087}O_{1.587}$: AIMD

- Simulations using VASP, 240 ps, 279 atoms, 3 temperatures

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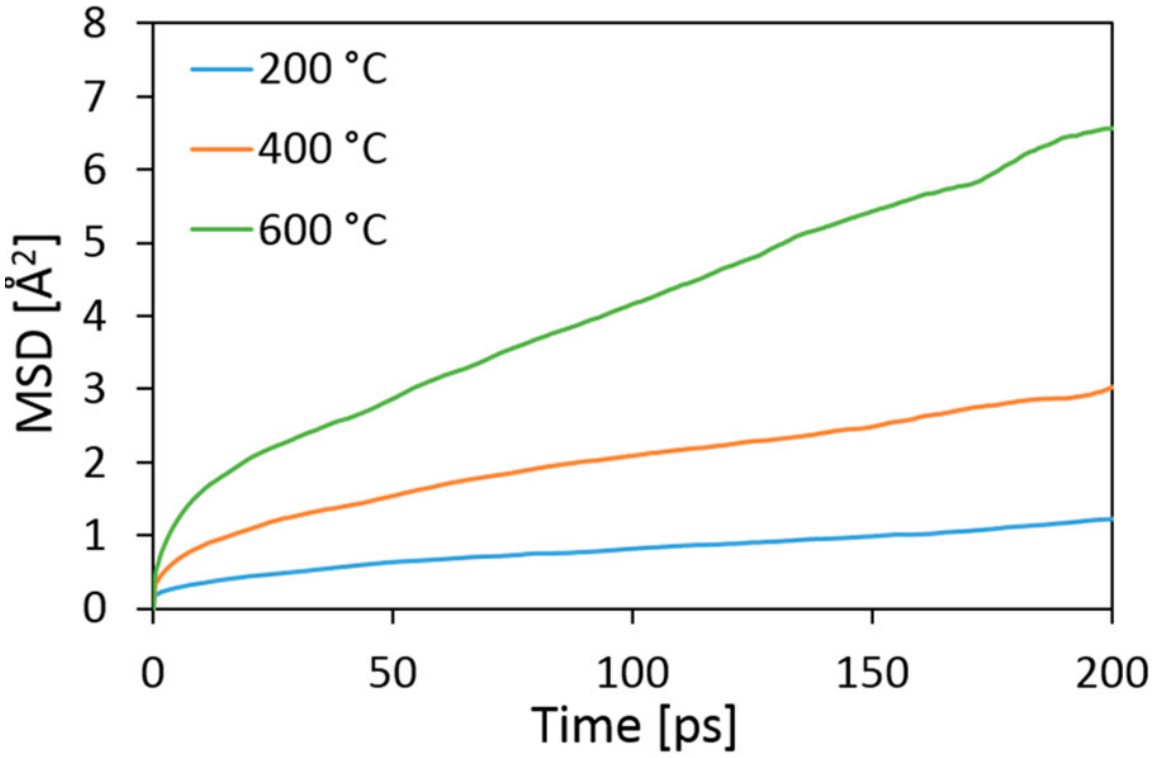
O mean square displacements



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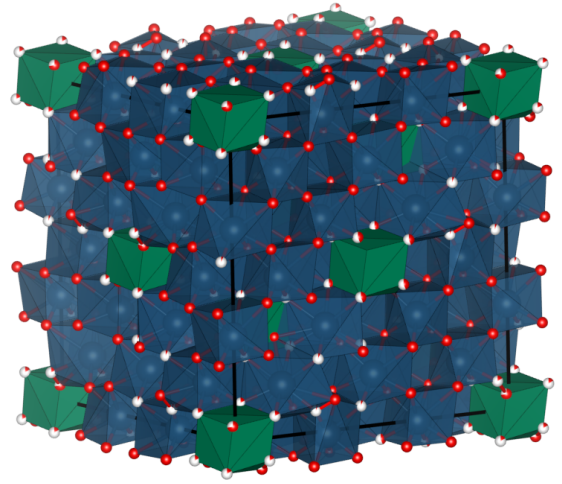
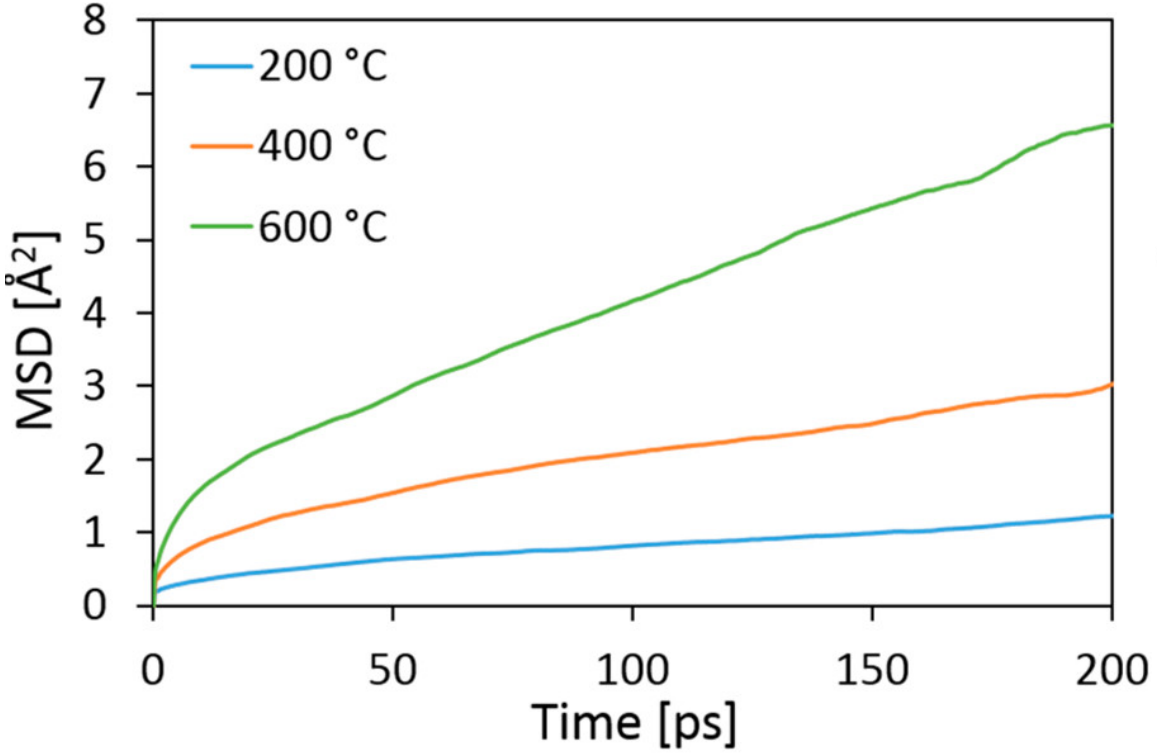
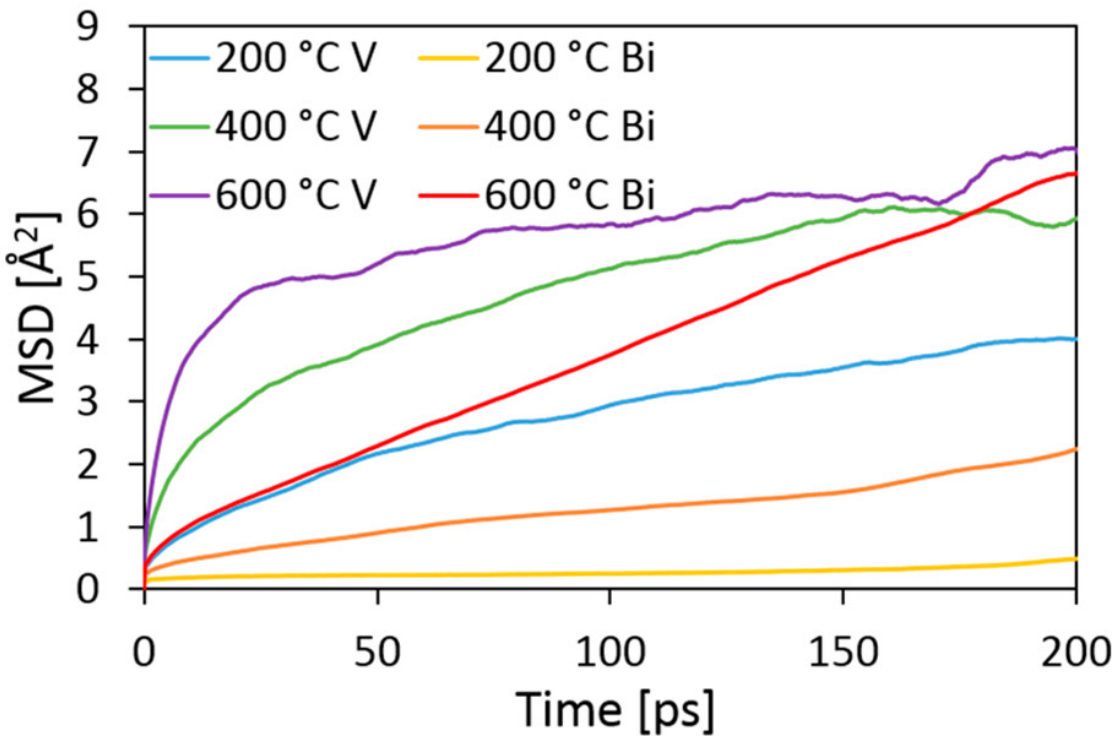


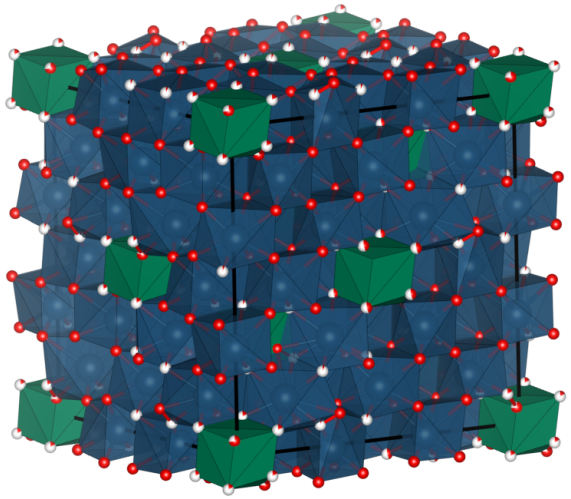
- Simulations using VASP, 240 ps, 279 atoms, 3 temperatures

O mean square displacements

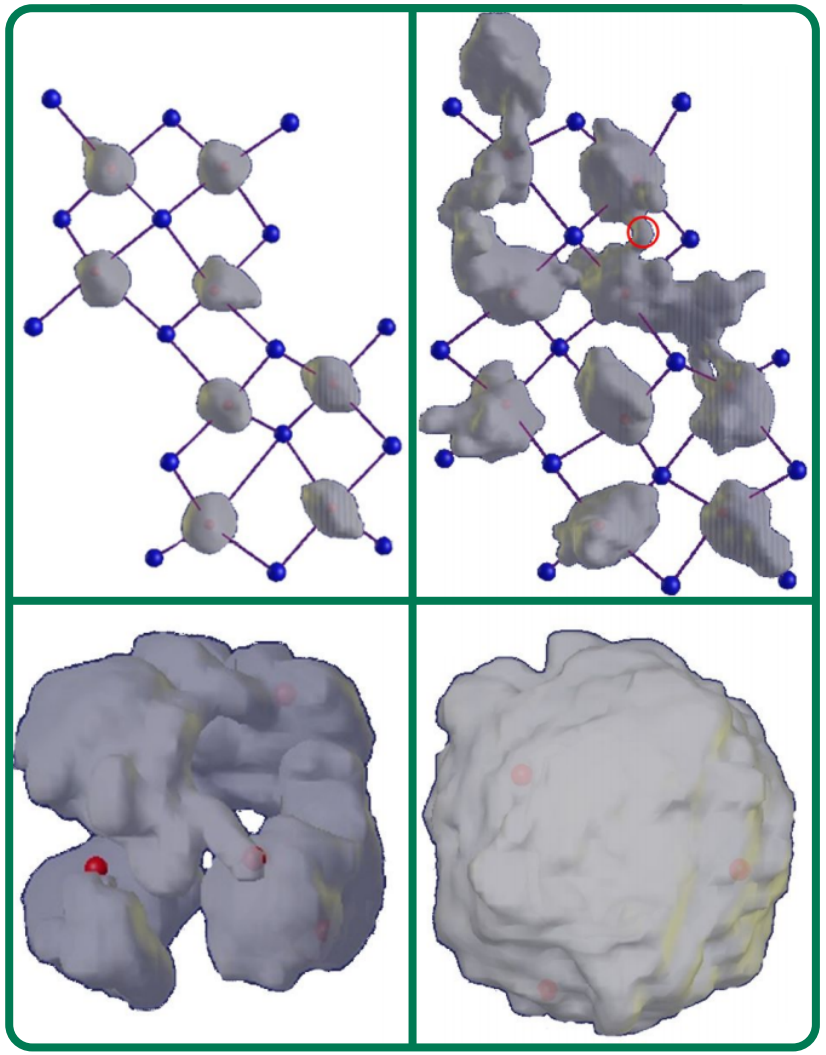




$Bi_{0.913}V_{0.087}O_{1.587}$: AIMD



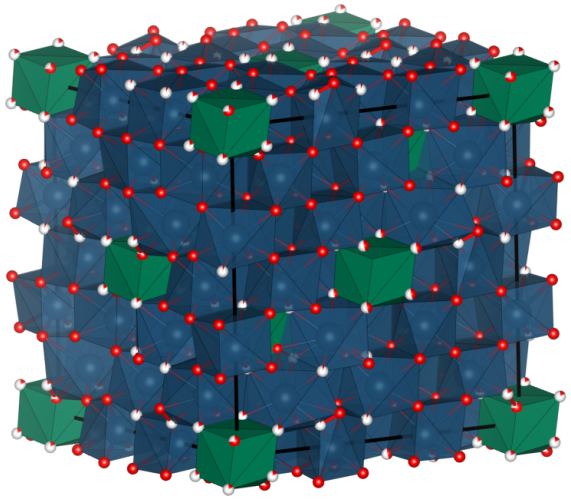
200 °C 600 °C

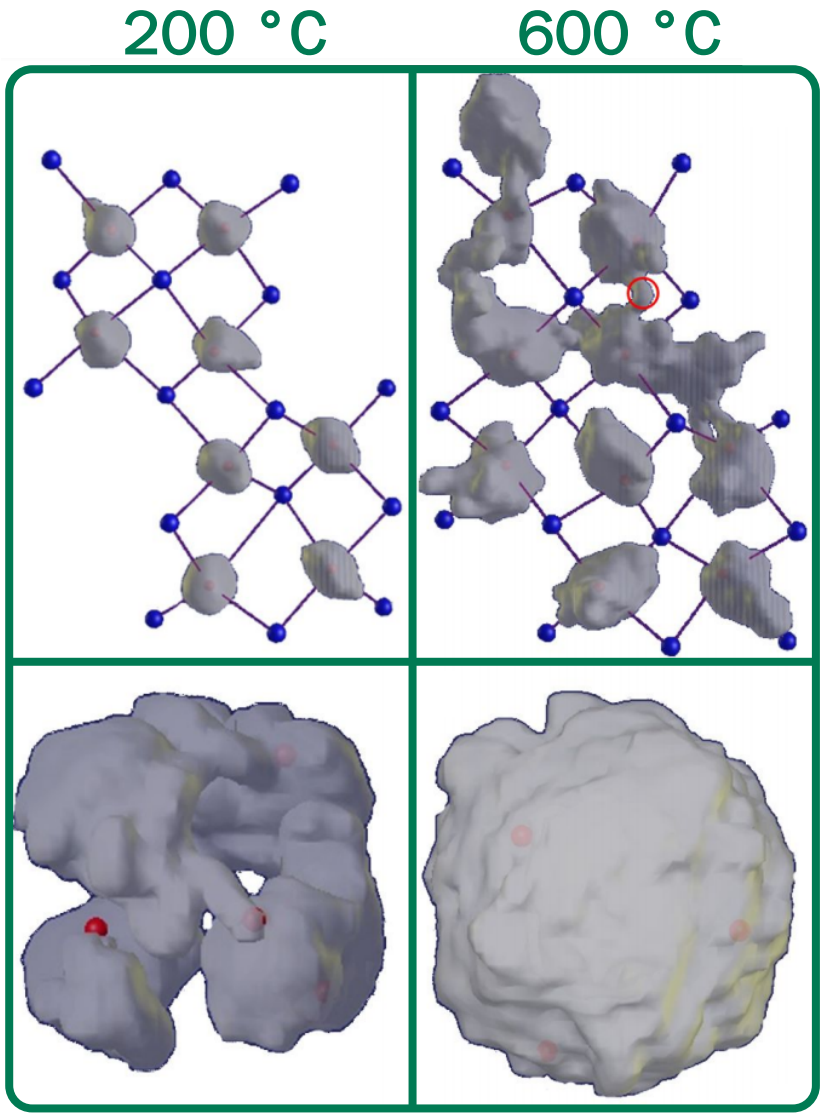


Bi-O sublattice
Long-range

V-O sublattice
Localised

$Bi_{0.913}V_{0.087}O_{1.587}$: AIMD





Bi-O sublattice

Long-range

E_a = 0.38(1) eV

V-O sublattice

Localised

E_a = 0.05(1) eV

$Bi_{0.913}V_{0.087}O_{1.587}$: AIMD

Jump type	Number of Jumps		
	200 °C	400 °C	600 °C
VO_x	339 (69.3%)	863 (59.3 %)	1062 (55.8%)
V–Bi / Bi–V	29 (8.0%)	143 (9.8%)	214 (11.3%)
Bi–O	111 (22.7%)	450 (30.9%)	628 (32.9%)
Total	489	1456	1904

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Recipe for Success

- Extended Bi-O network
- Variable V^{5+} coordination
- Facile localised motion

Summary

- Observed conduction process with QENS
- Simulated same process with MD
- MD revealed additional localised motion
- Identified key structural features
- Use them to develop better conductors