From Total Scattering to Total Understanding: Structure-Functionality Relationships in Scheelite-Type Oxides

Presented by:

Mr Bryce Mullens

University of Sydney / Université Paris-Saclay

PhD Candidate in Solid-State / Materials Chemistry

ADD2022 – Wednesday 19th October 2022

THE UNIVERSITY OF SYDNEY

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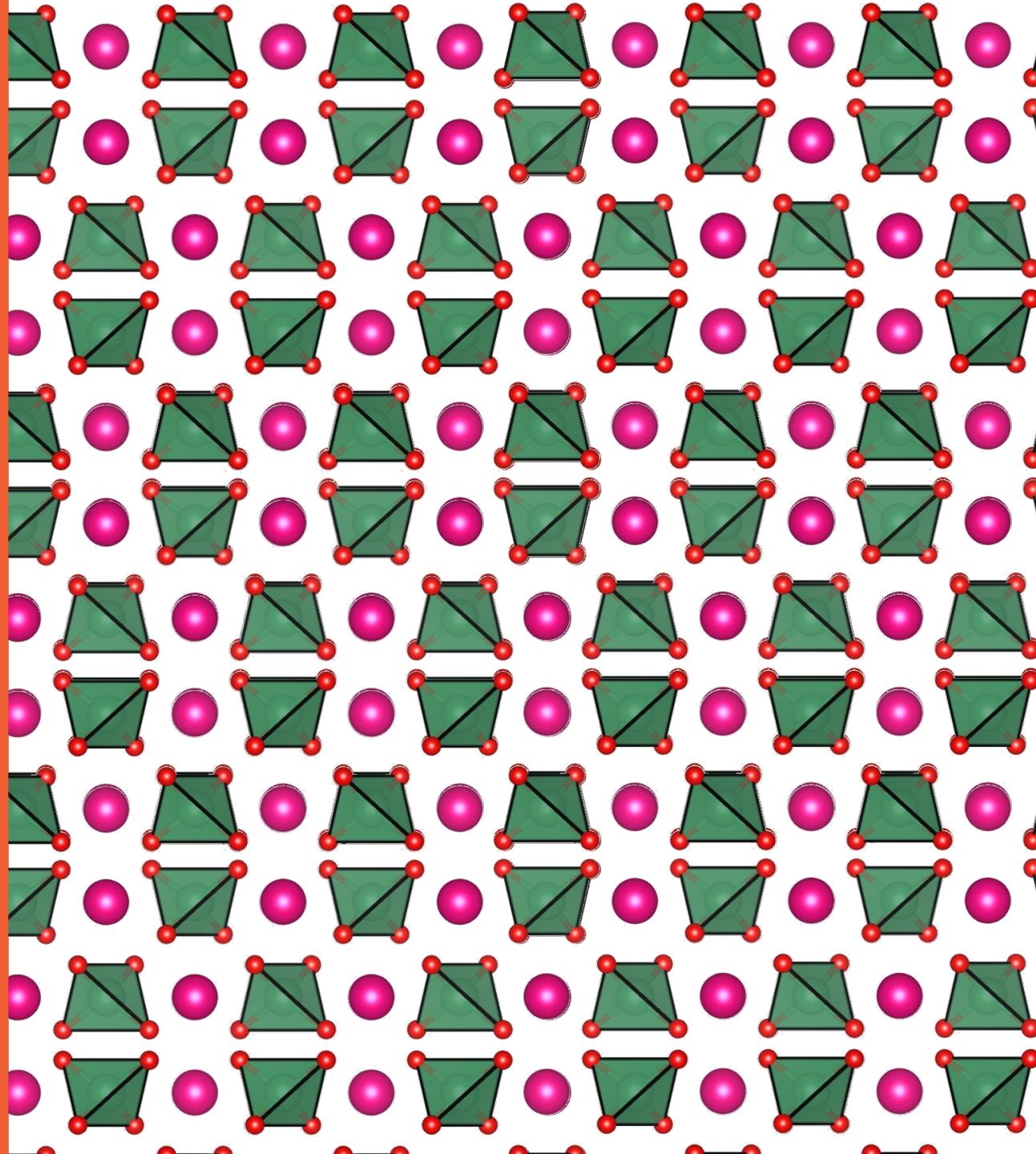


Thank You!

Supervisors

- Prof Brendan J. Kennedy
- Prof Chris Ling
- Dr Zhaoming Zhang
- Prof Gianguido Baldinozzi
- Prof Karena Chapman
- Prof Maik Lang

Postdocs

- Dr Matilde Saura Múzquiz
- Dr Fred Marlton

Oak Ridge National Laboratory

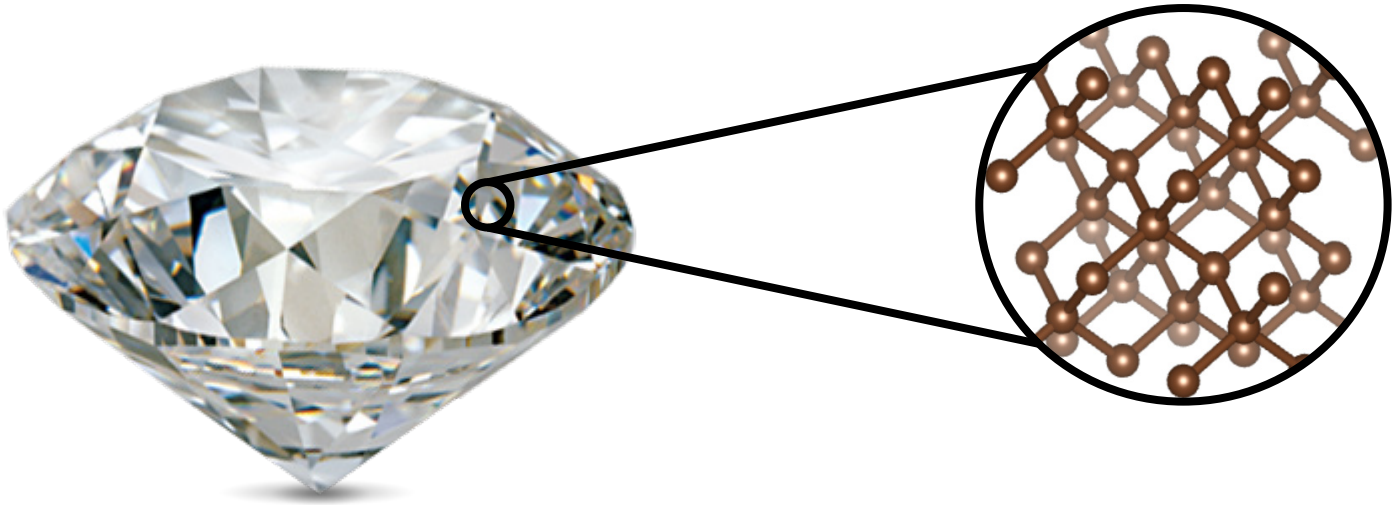
- Dr Alicia Manjon-Sanz
- Dr Joerg Neuefeind
- Dr Michelle Everett

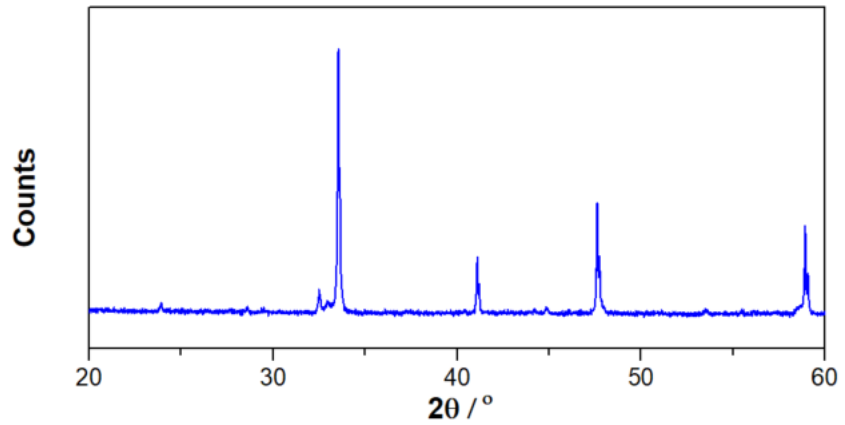
Diamond Light Source

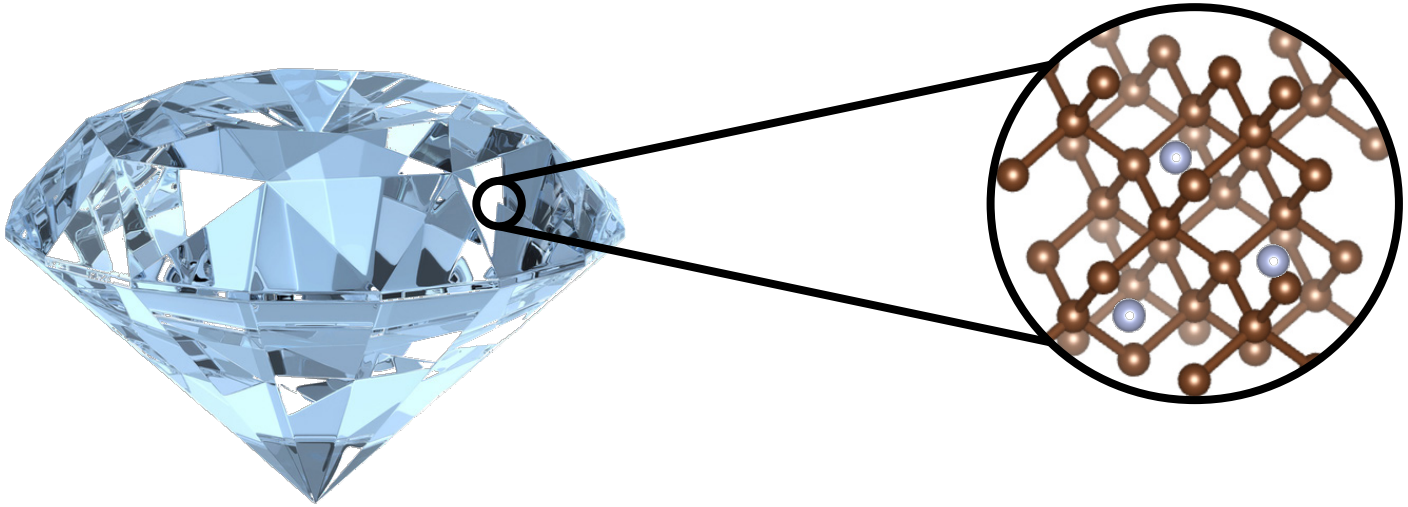
- Dr Phil Chater

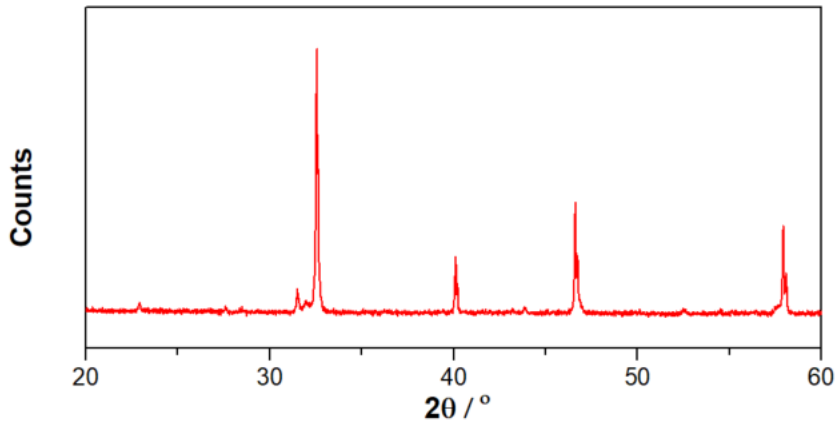
The University of Sydney Solid-State Research Group

Structures and Properties of Diamond

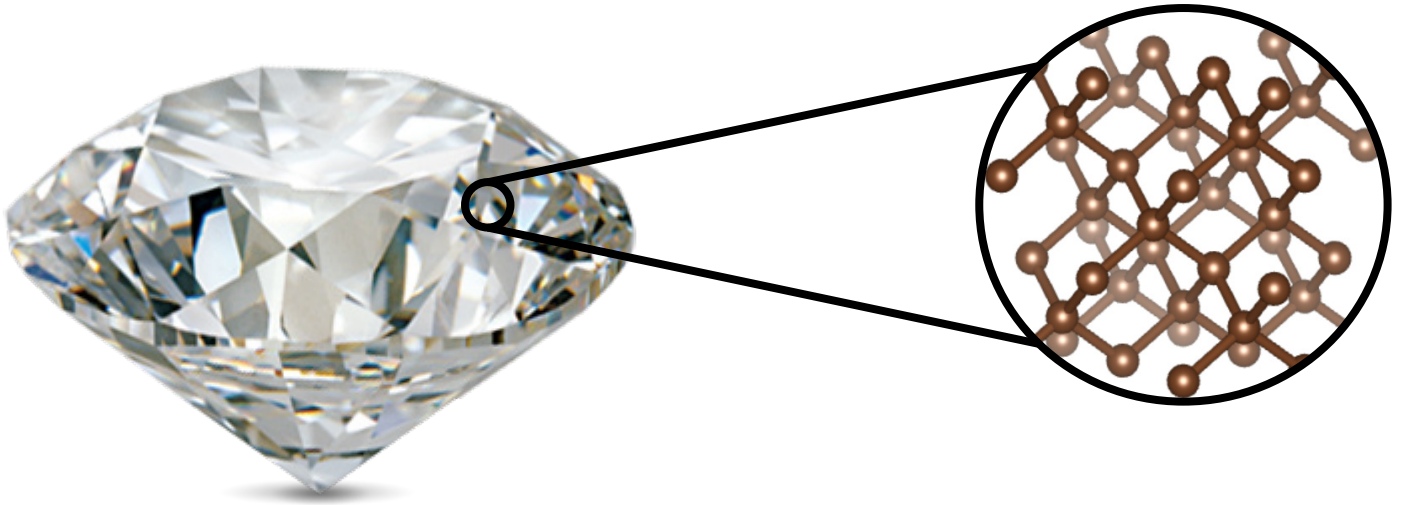


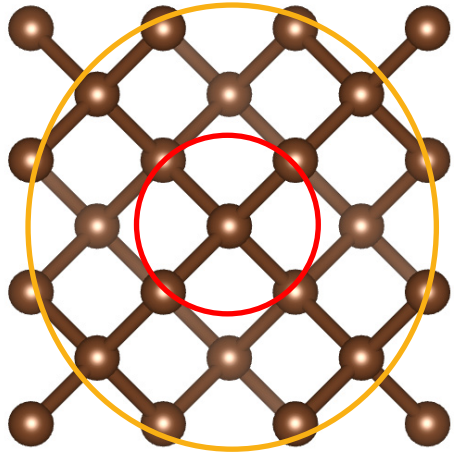


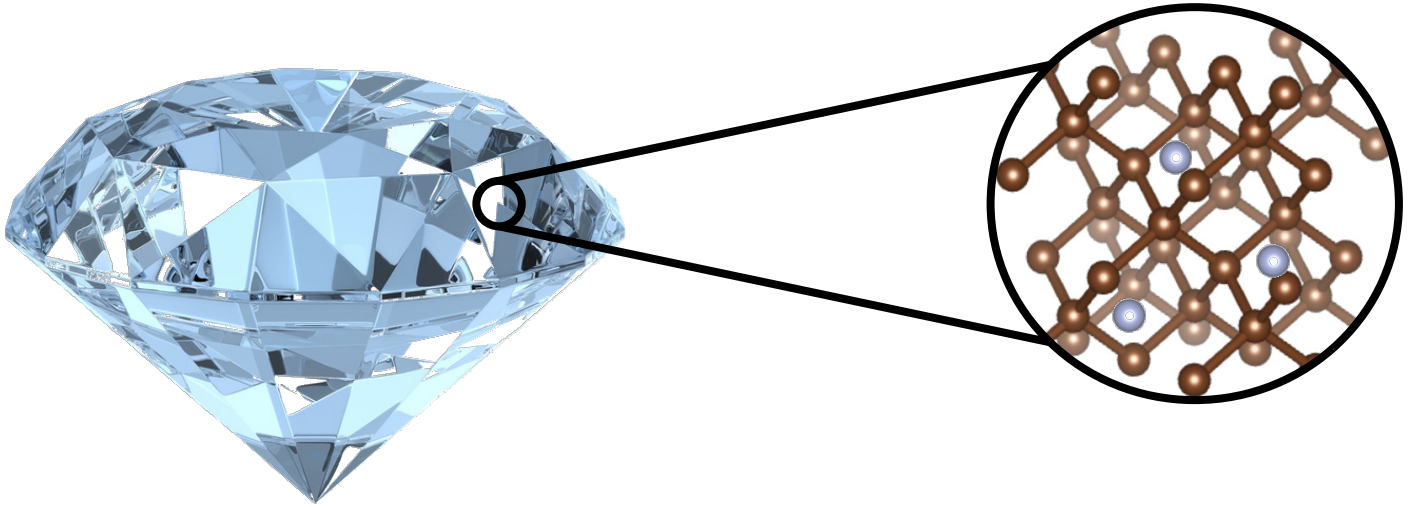


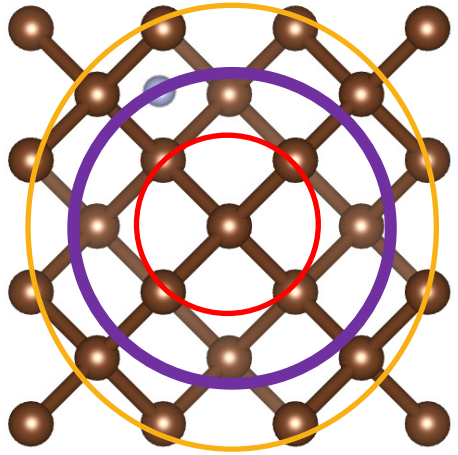


Structures and Properties of Diamond

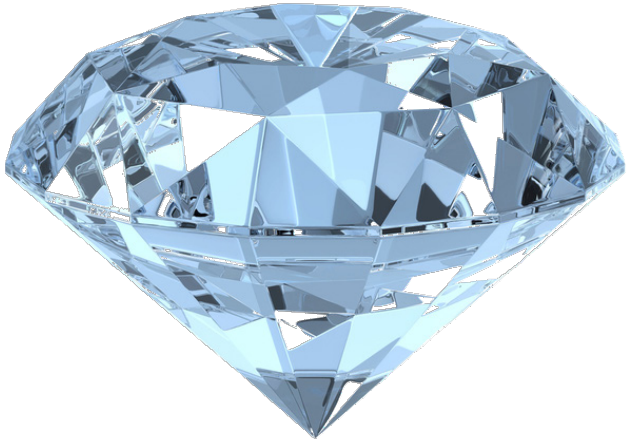


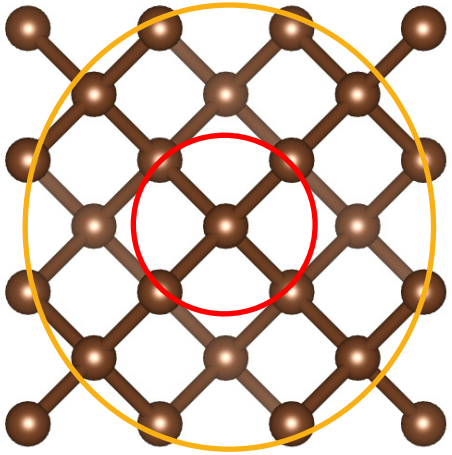


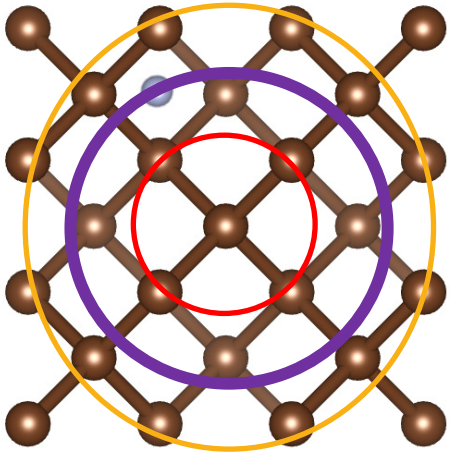


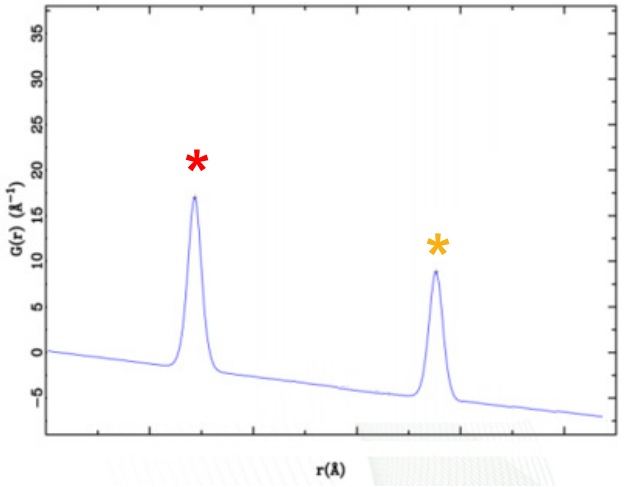


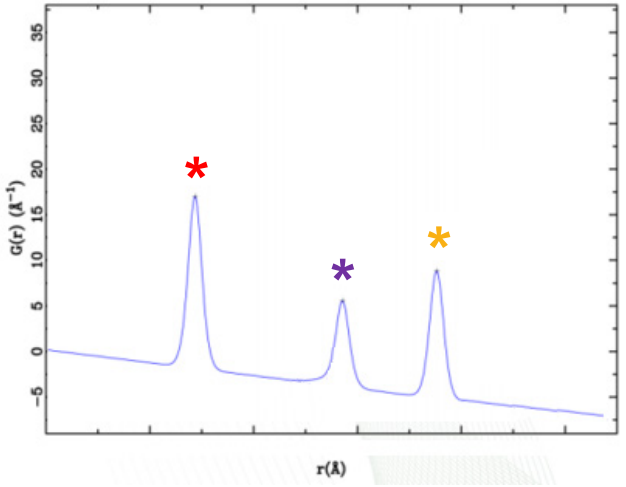
Structures and Properties of Diamond



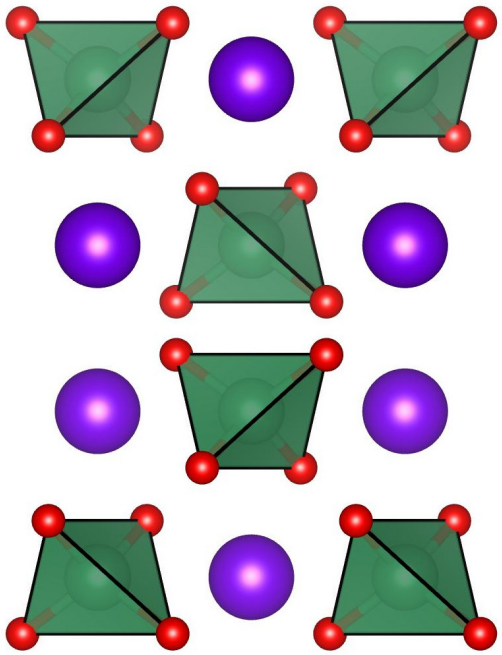








The Wonderous ABO_4 Structure



ABO_4
Tetragonal Scheelite

1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
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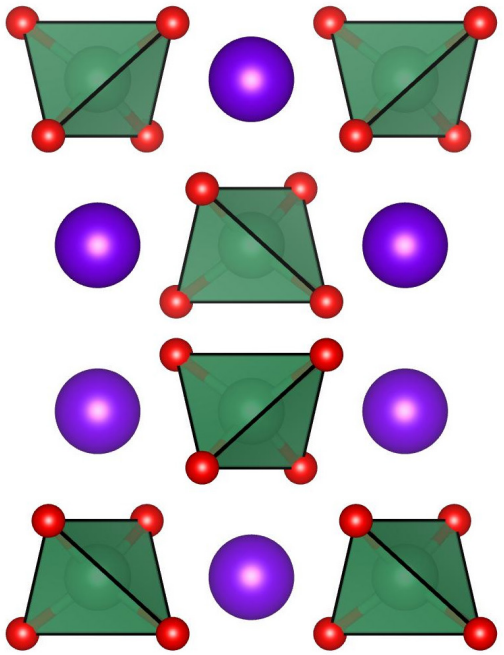

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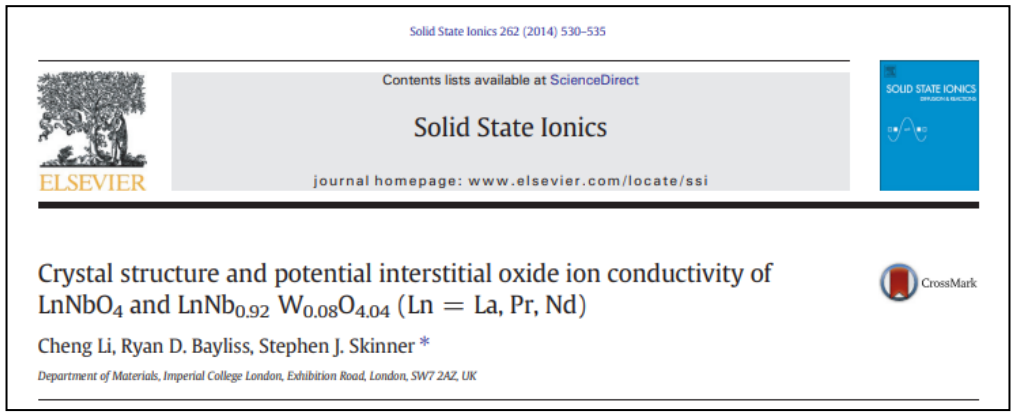


Solid State Ionics 262 (2014) 530–535

Contents lists available at ScienceDirect

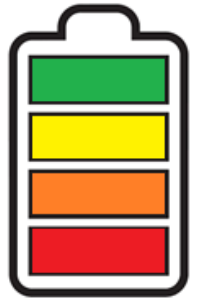
Solid State Ionics

journal homepage: www.elsevier.com/locate/ssi

Crystal structure and potential interstitial oxide ion conductivity of $LnNbO_4$ and $LnNb_{0.92}W_{0.08}O_{4.04}$ (Ln = La, Pr, Nd)

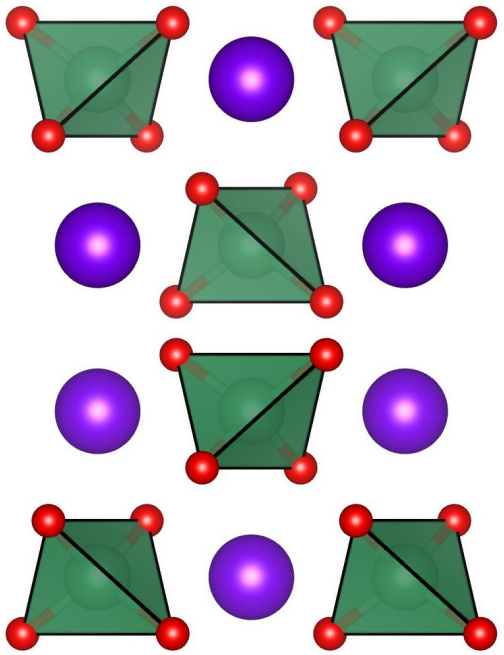
Cheng Li, Ryan D. Bayliss, Stephen J. Skinner *

Department of Materials, Imperial College London, Exhibition Road, London, SW7 2AZ, UK



Li *et al.*; *Solid State Ionics*, **2014**, *262*, 530-535.

The Wonderous ABO_4 Structure



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Materials Research Bulletin 61 (2015) 422–432

Contents lists available at ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

Scheelite-type MWO_4 (M = Ca, Sr, and Ba) nanophosphors: Facile synthesis, structural characterization, photoluminescence, and photocatalytic properties

C. Shivakumara [a,*], Rohit Saraf [b], Sukanti Behera [a], N. Dhananjaya [c], H. Nagabhushana [d]

Shivakumara *et al.*; *Mater. Res. Bull.*, **2015**, *61*, 422-432.

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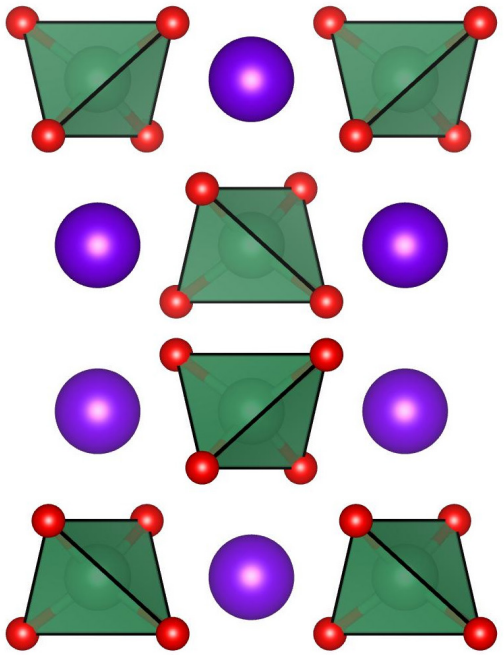

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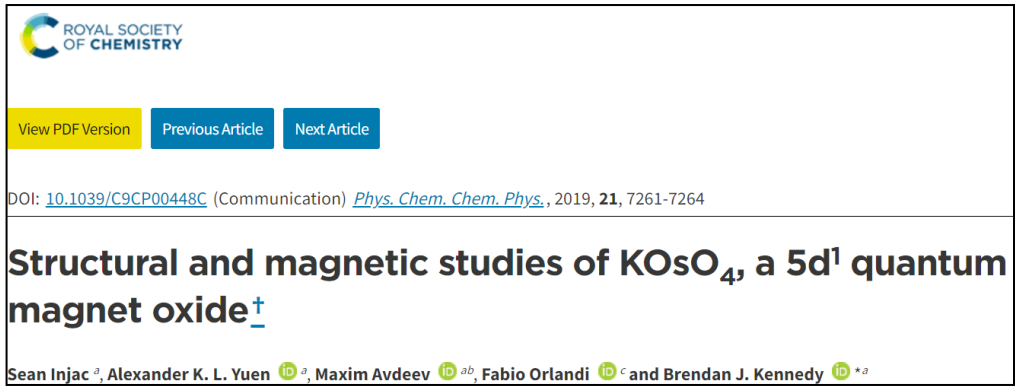
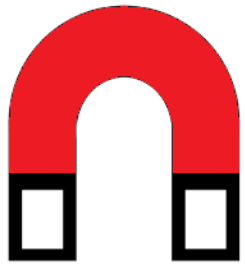
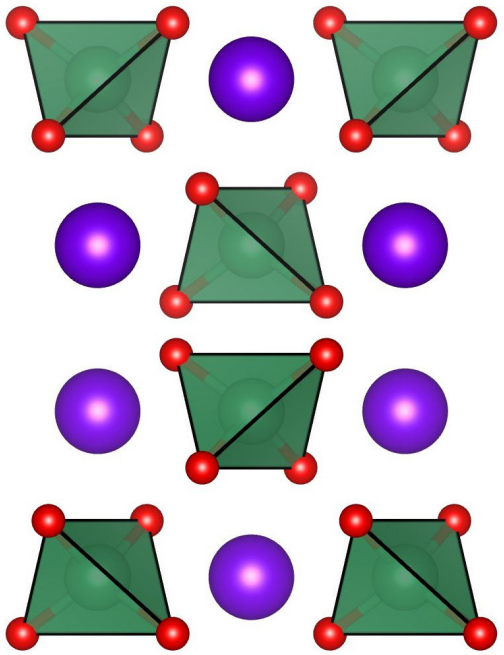




Injac *et al.*; *Phys. Chem. Chem. Phys.*, **2019**, *21*, 7261-7264.

The Wonderous ABO_4 Structure



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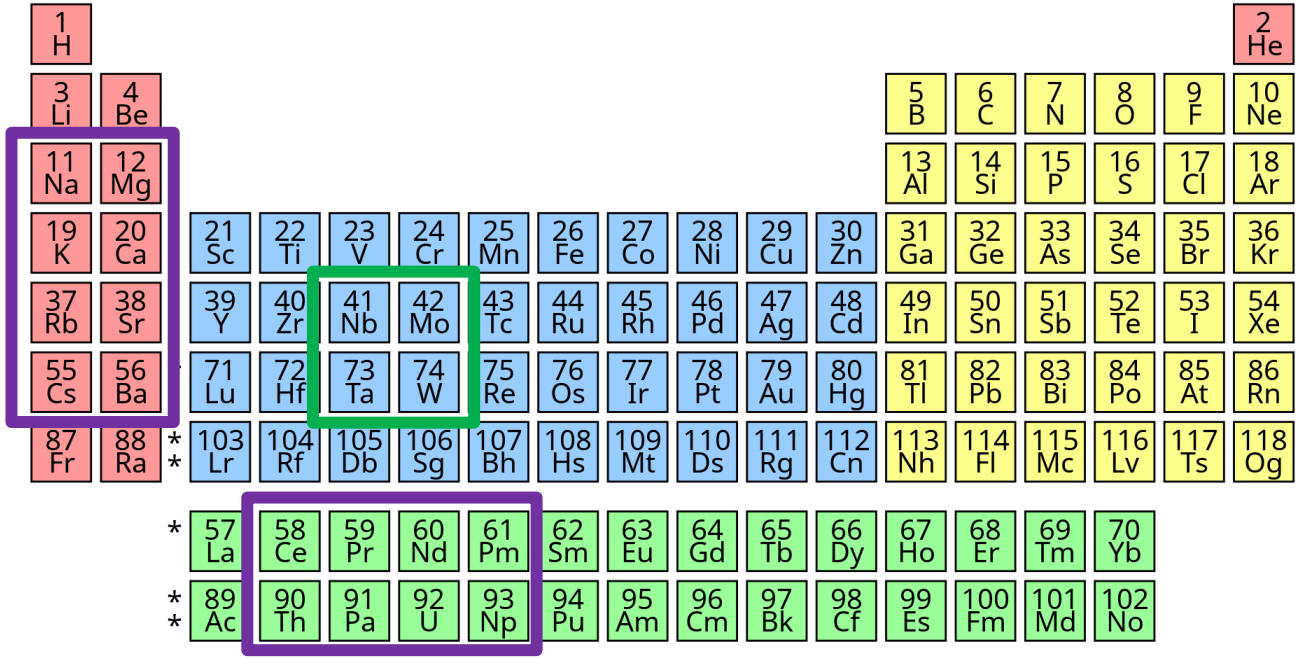

Fonteneau *et al.*; *Mater. Res. Bull.*, **1977**, *12* (1), 25-33.

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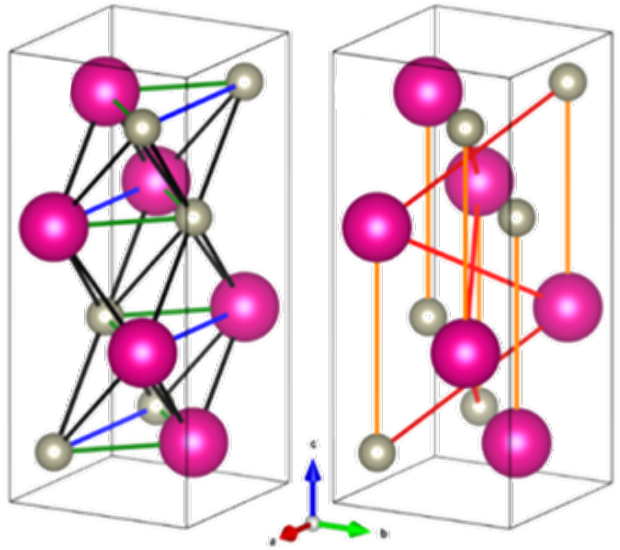
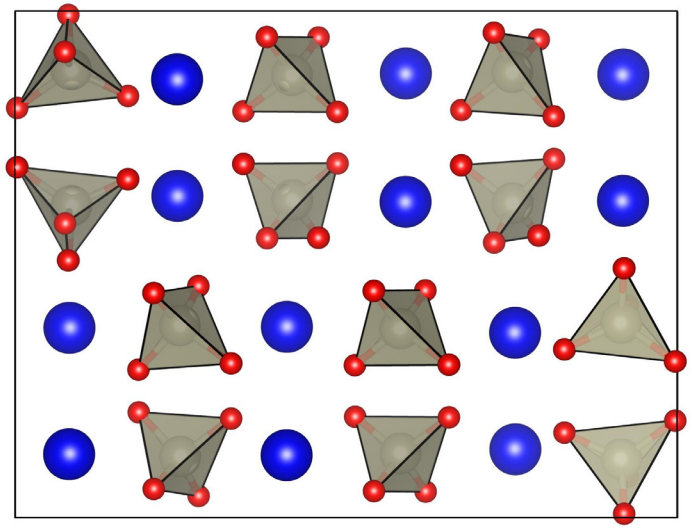
Today's Outline

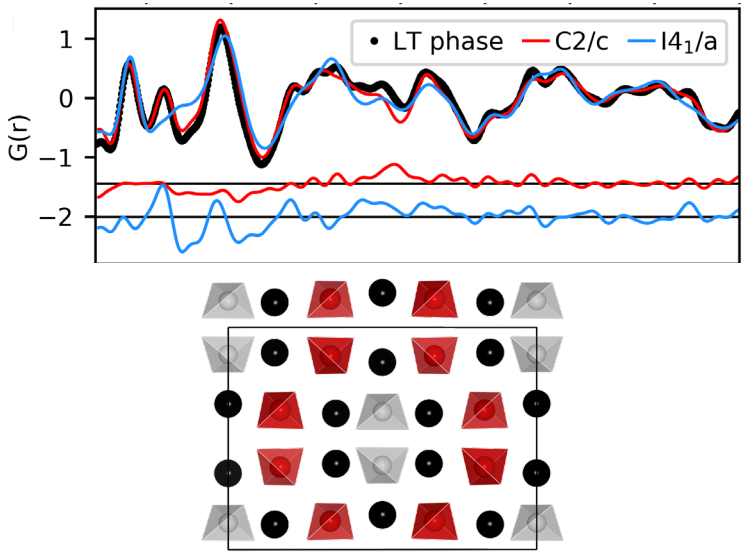
High-Temperature Phase Transition in $RbReO_4$



Re-Entrant Phase Transition in $TlReO_4$



Symmetry-Lowering in $Bi_3FeMo_2O_{12}$

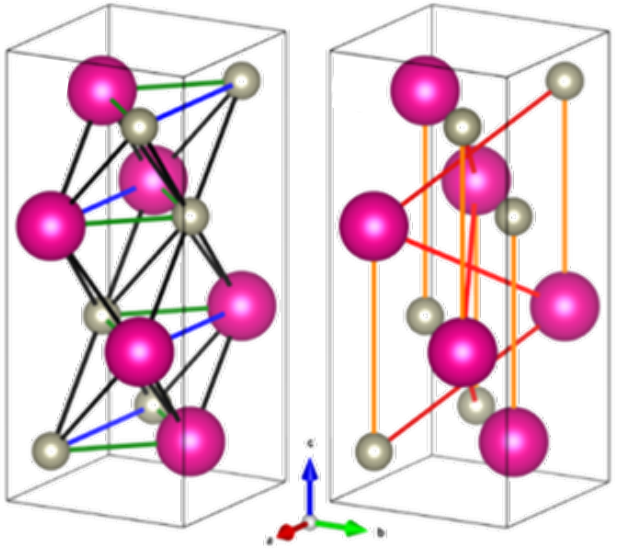


THE UNIVERSITY OF SYDNEY

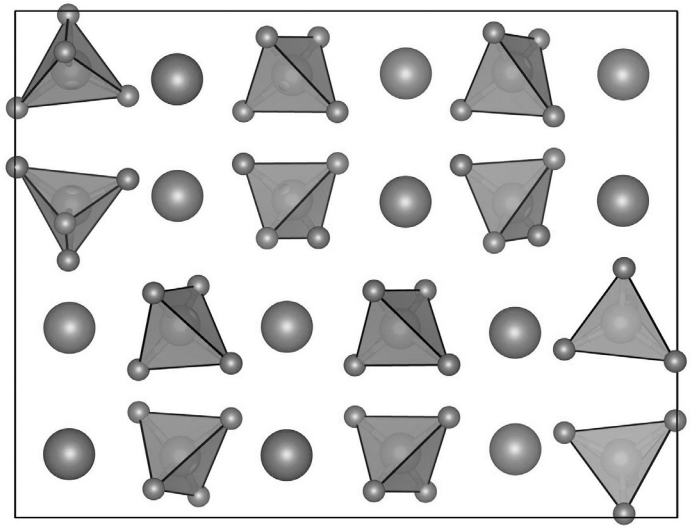
Today's Outline

High-Temperature Phase Transition in $RbReO_4$

Why do the Re-O bonds decrease upon heating?



Re-Entrant Phase Transition in $TlReO_4$



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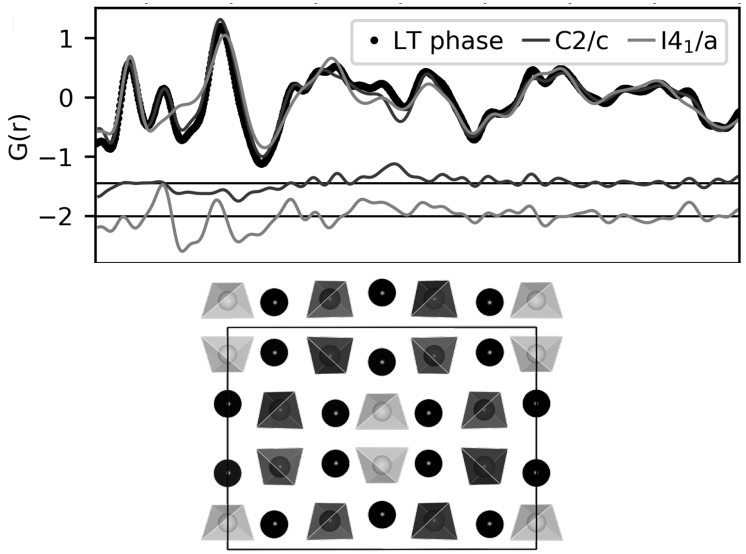
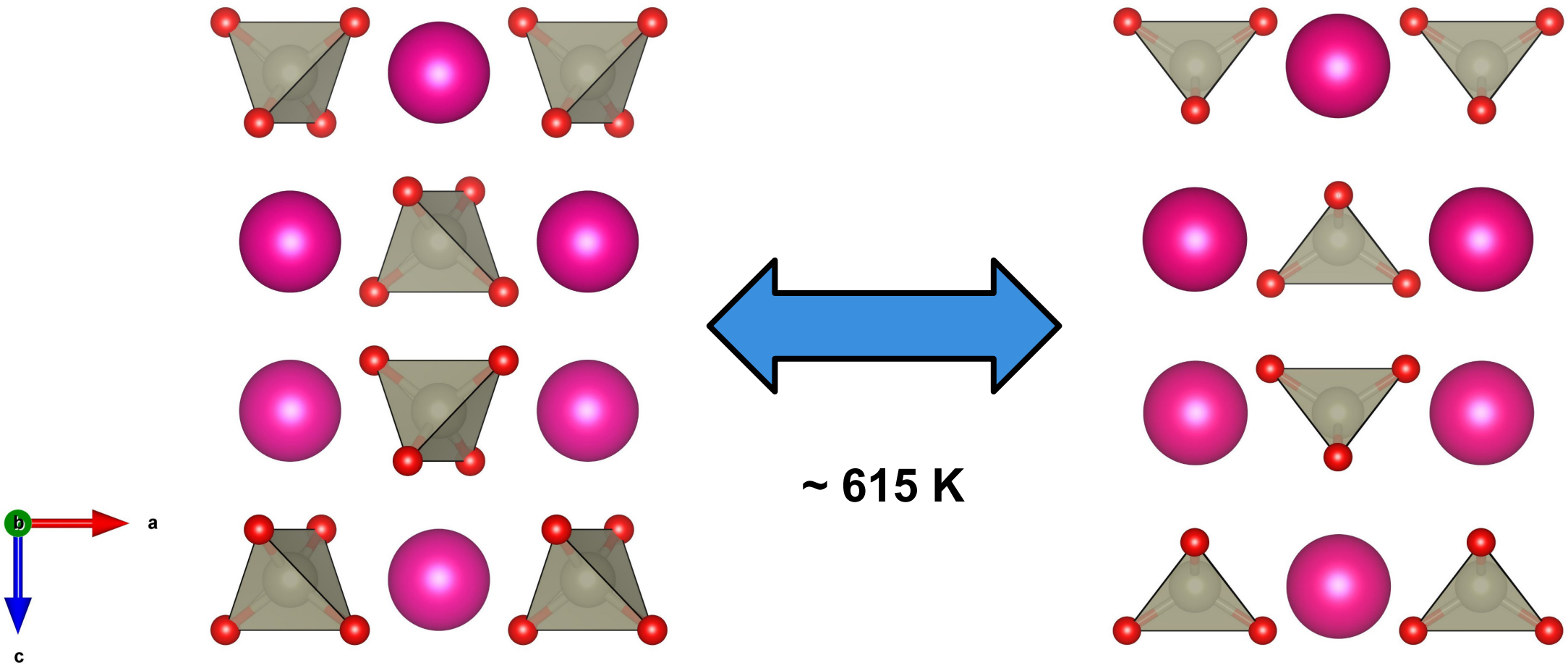


Phase Transition in $RbReO_4$



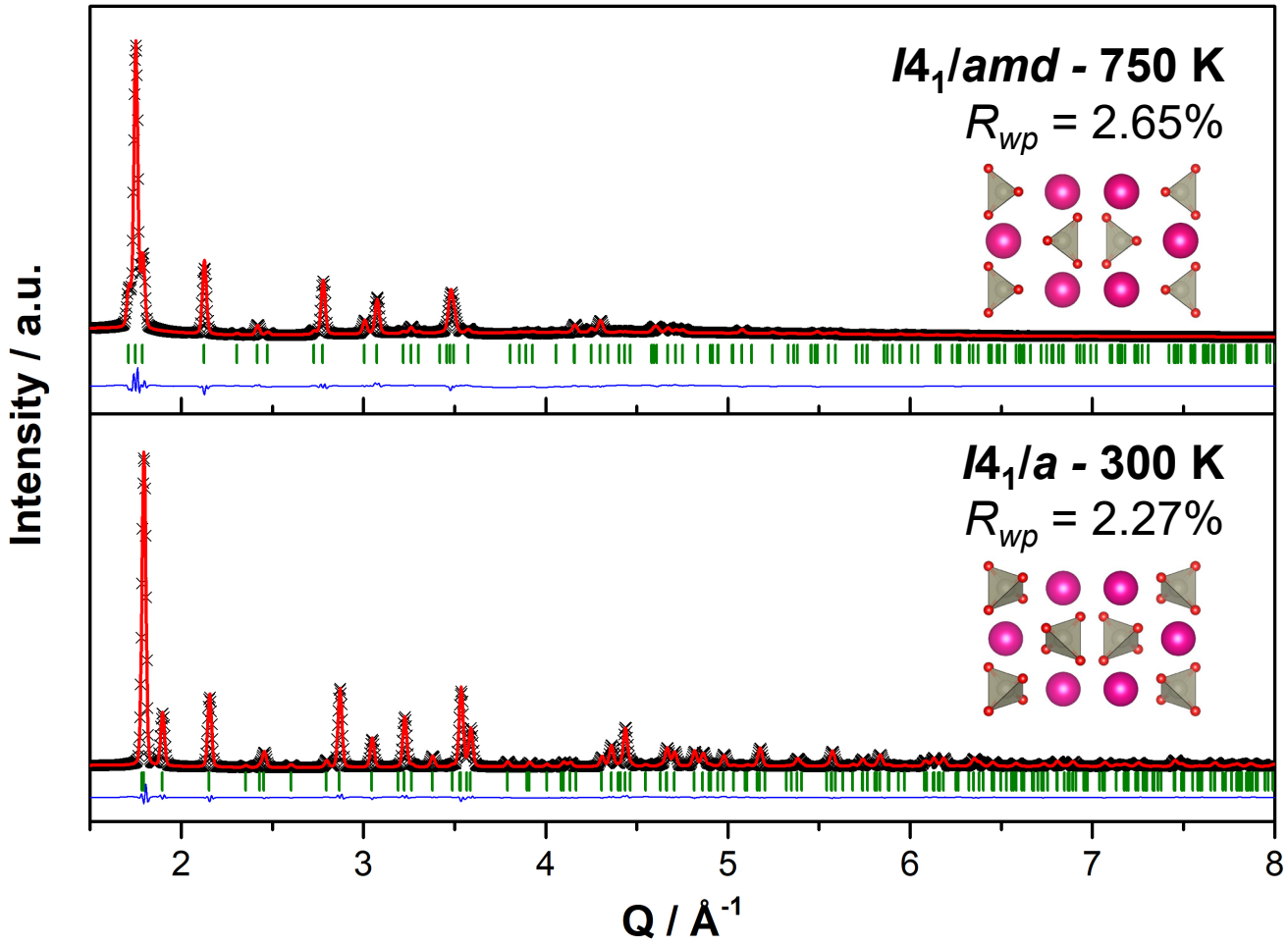
$I4_1/a$
Tetragonal Scheelite

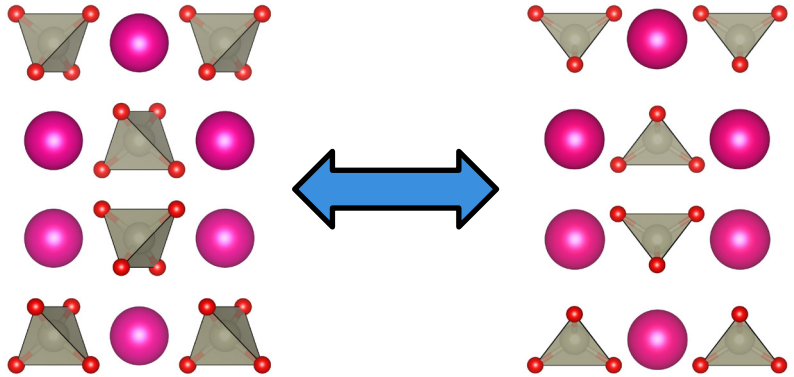
$I4_1/amd$
Scheelite Aristotype

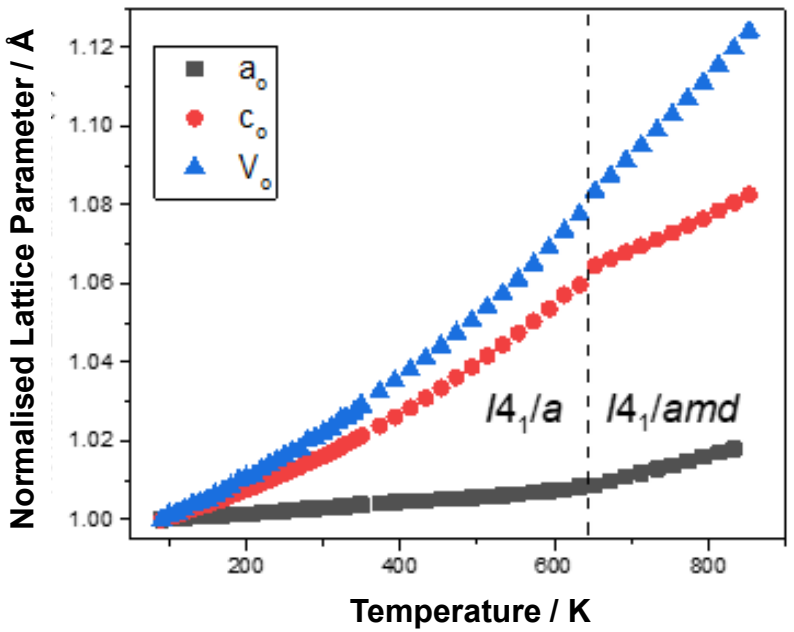
Chay *et al.*; *Dalton Trans.*, **2019**, *48*, 17524.

Phase Transition in $RbReO_4$

SXRD, λ = 0.16166 Å

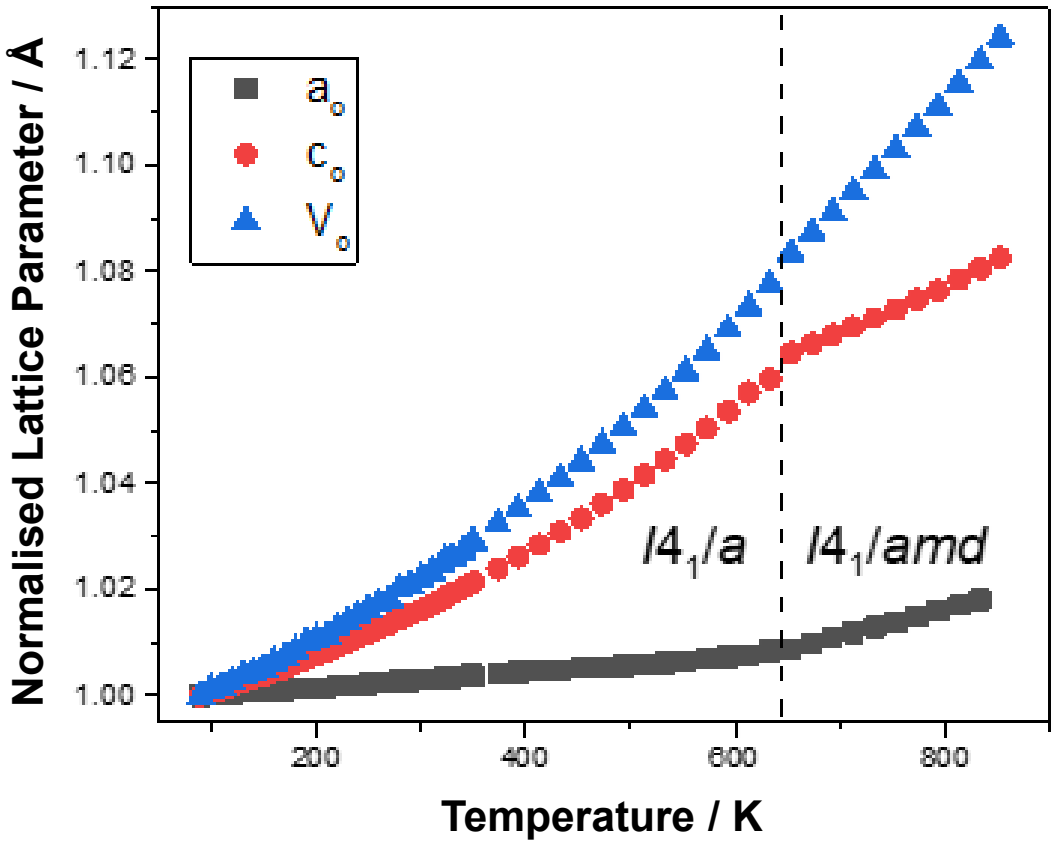


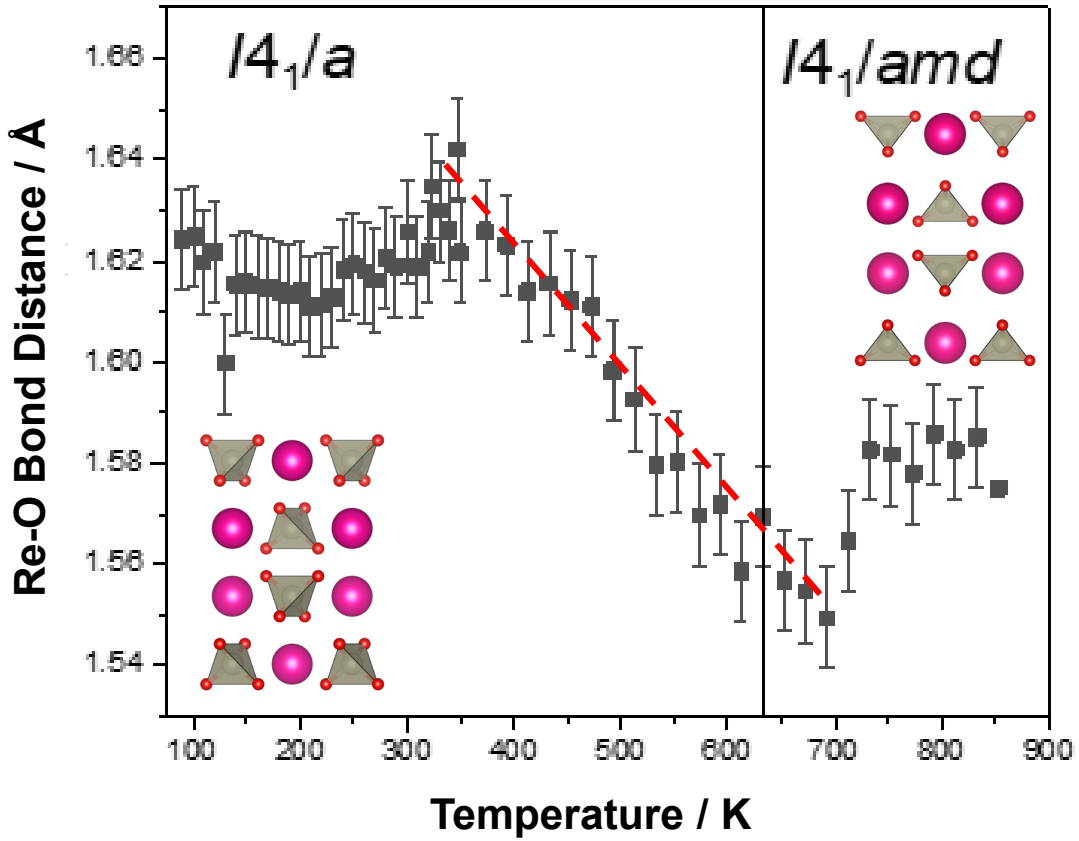




Marlton, Mullens *et al.*; *Inorg. Chem.*, **2022**, *61* (38), 15130-15137.

Irregularities in the Long-Range Structure

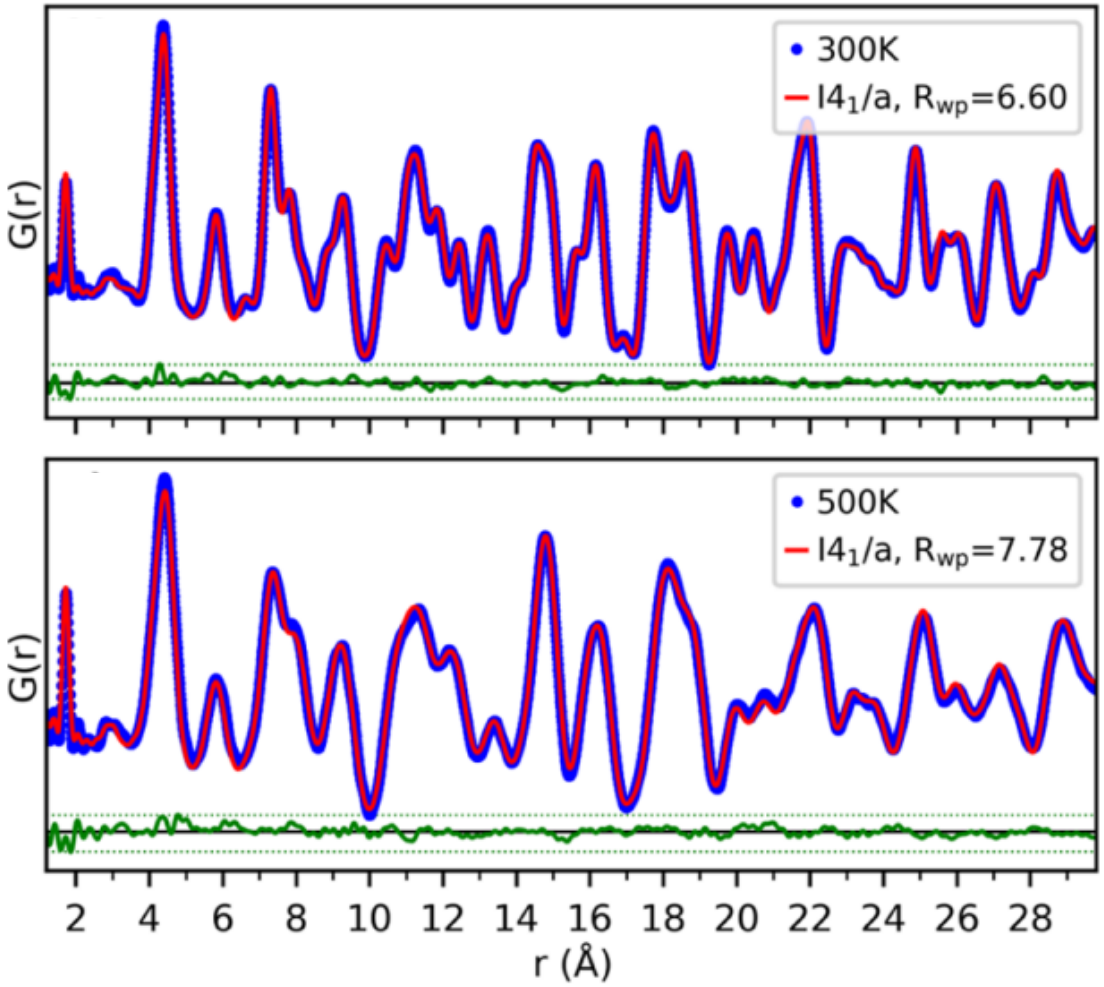


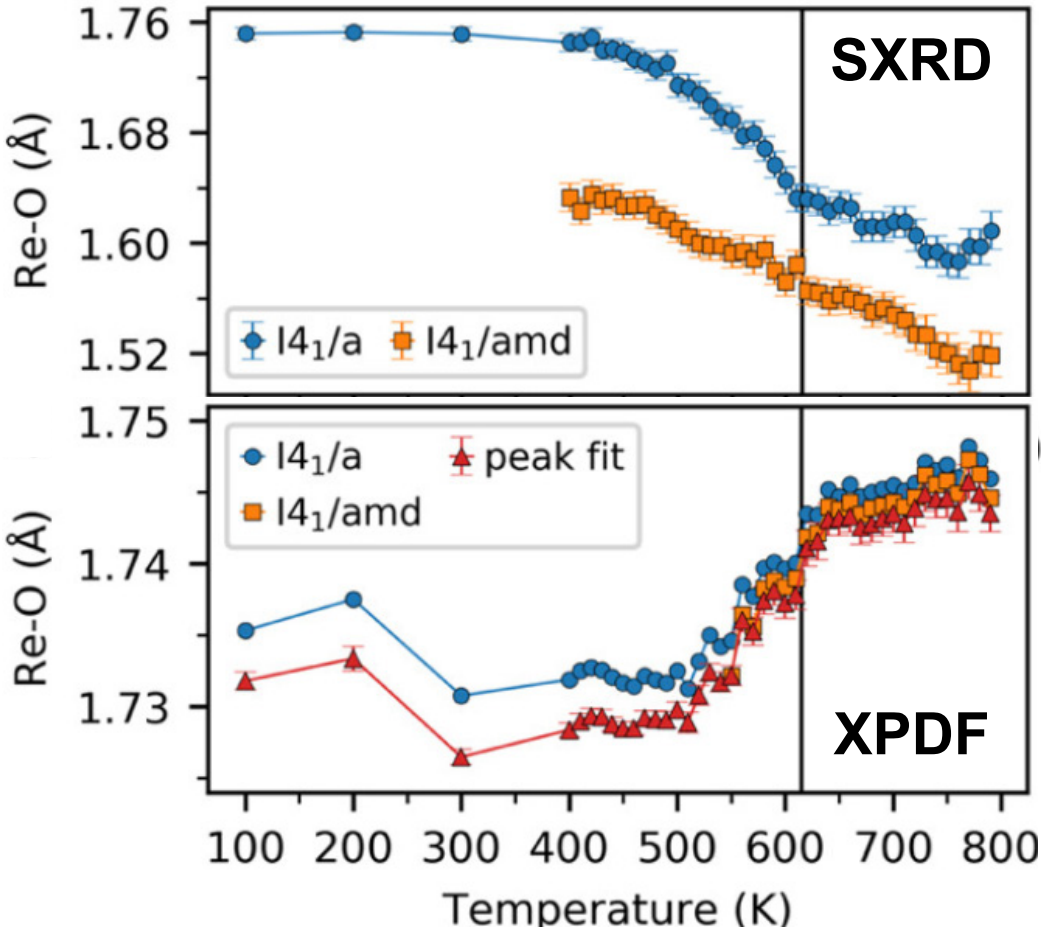


Marlton, Mullens *et al.*; *Inorg. Chem.*, **2022**, *61* (38), 15130-15137.

Local Structure of $RbReO_4$

X-Ray Pair Distribution Function Analysis





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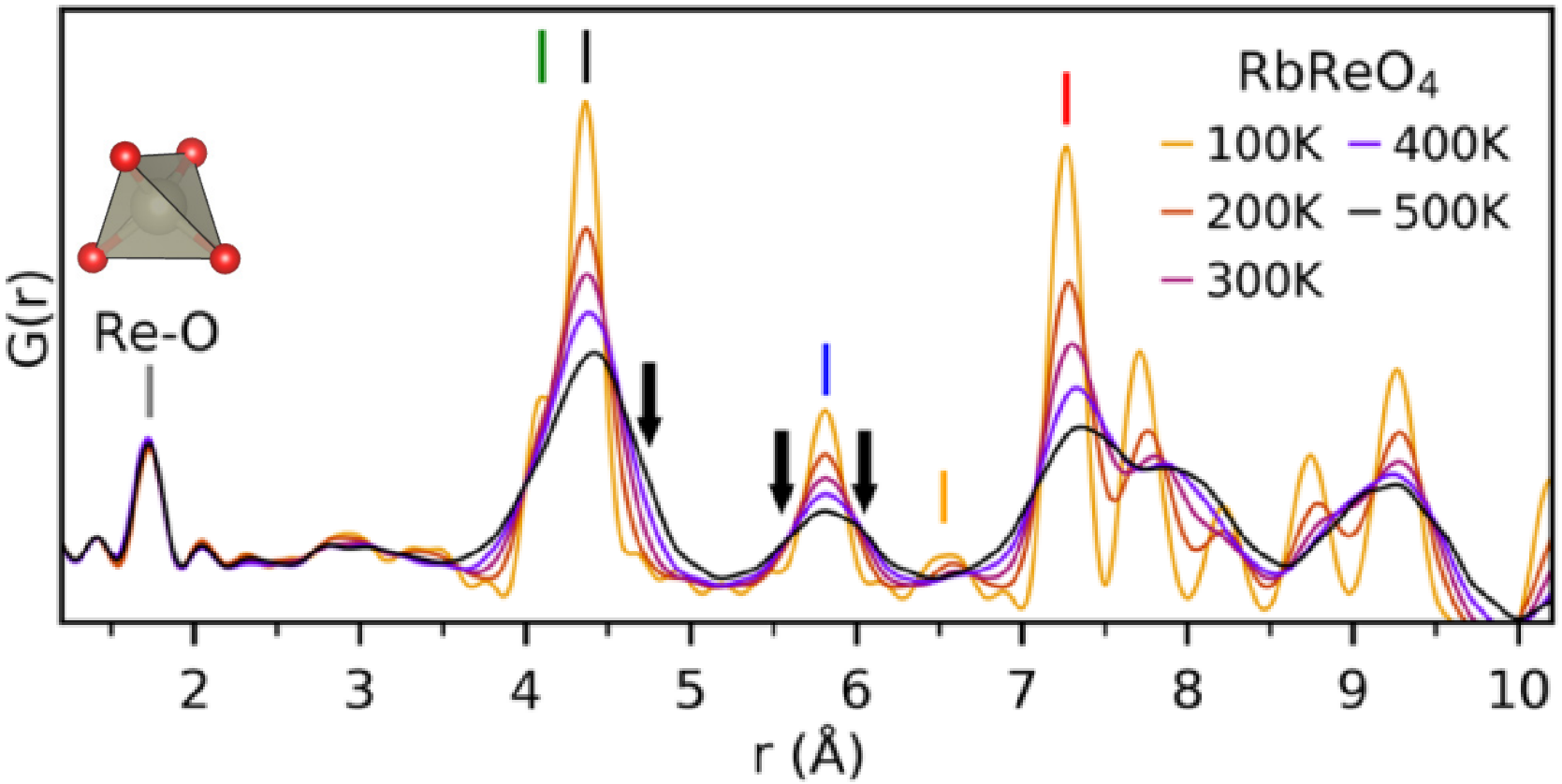

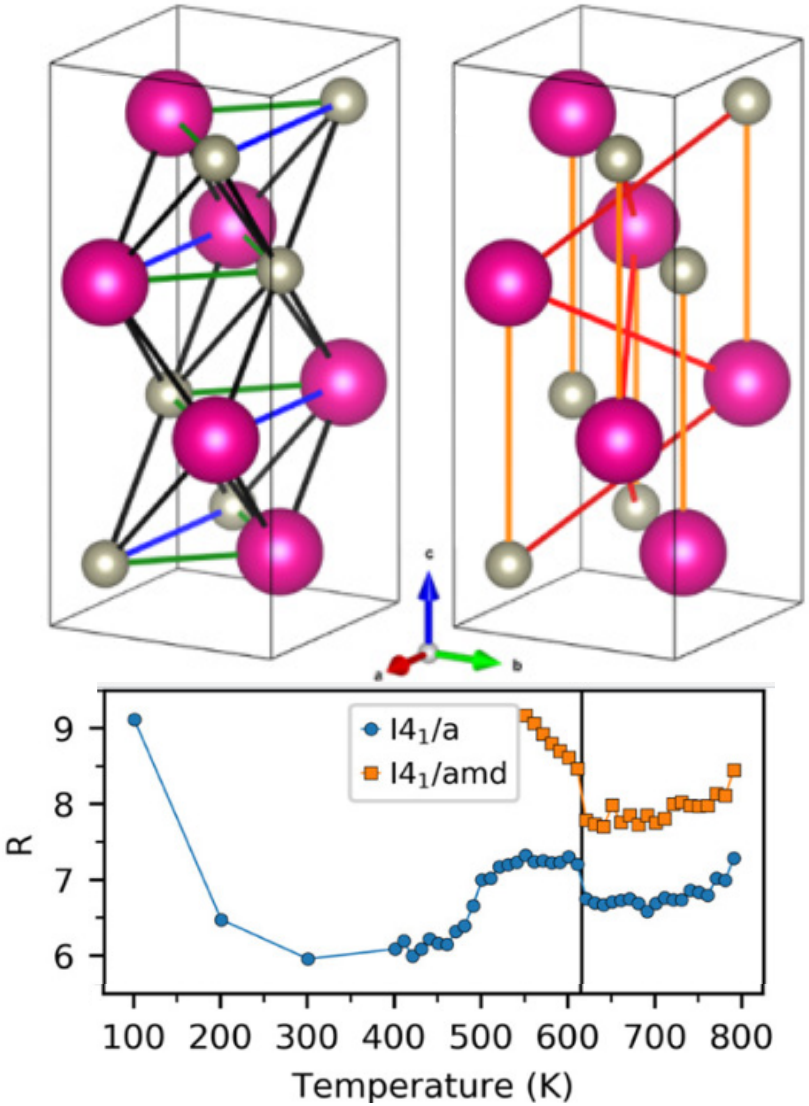

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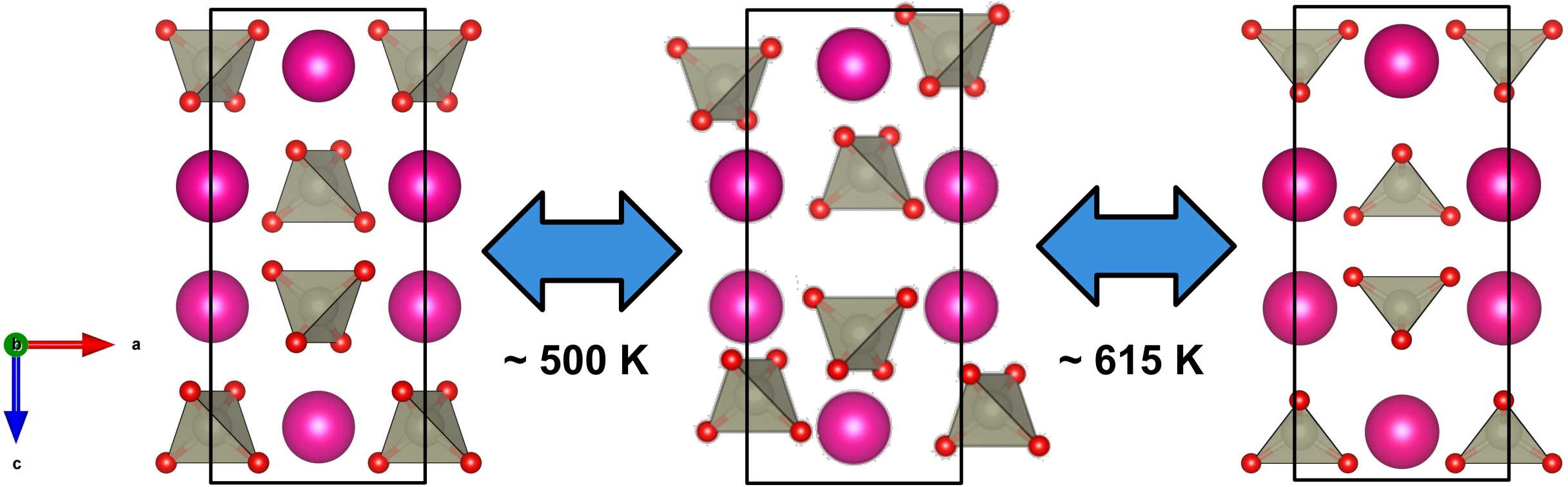
Local Displacements of ReO_4 Tetrahedra



$I4_1/a$
Tetragonal Scheelite

Long Range: $I4_1/a$
Local Static Tetrahedra Displacements

$I4_1/amd$
Scheelite Aristotype
Local Dynamic Disorder

Marlton, Mullens *et al.*; *Inorg. Chem.*, **2022**, *61* (38), 15130-15137.

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Today's Outline

High-Temperature Phase Transition in $RbReO_4$

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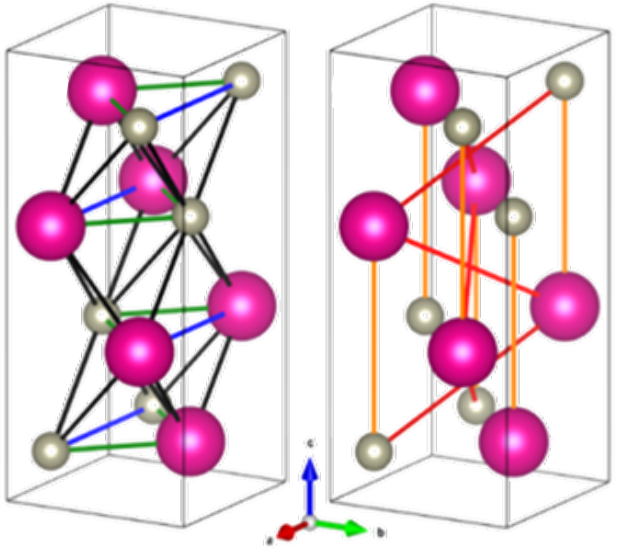
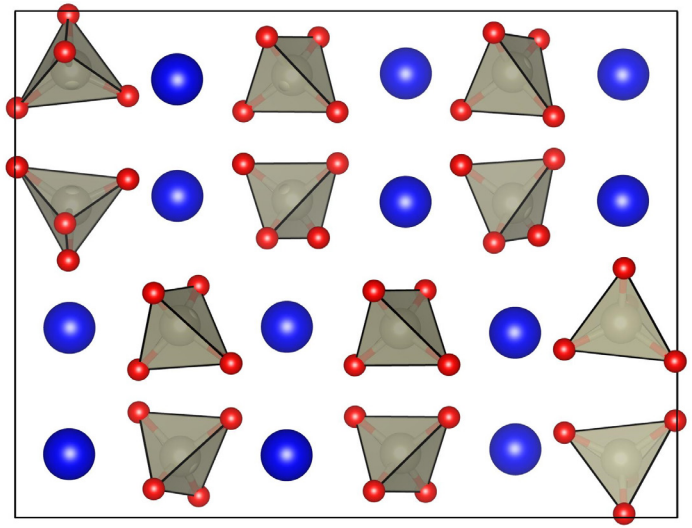
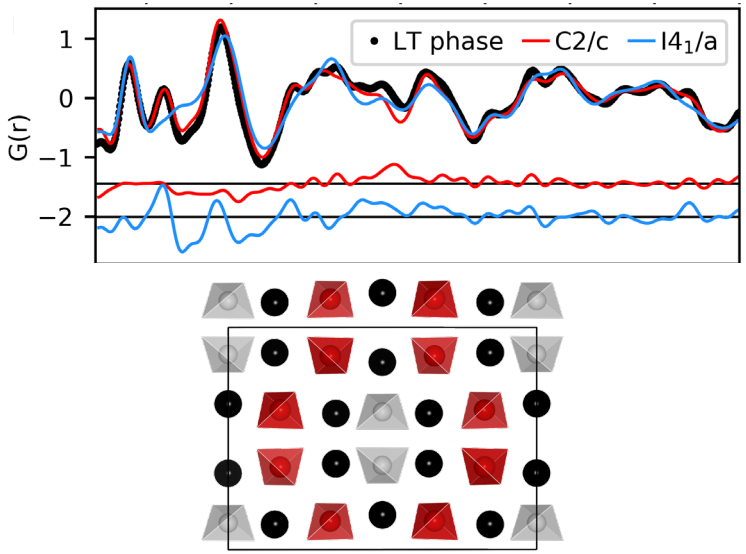


Local displacements of the ReO_4 tetrahedra.

Re-Entrant Phase Transition in $TlReO_4$



Symmetry-Lowering in $Bi_3FeMo_2O_{12}$



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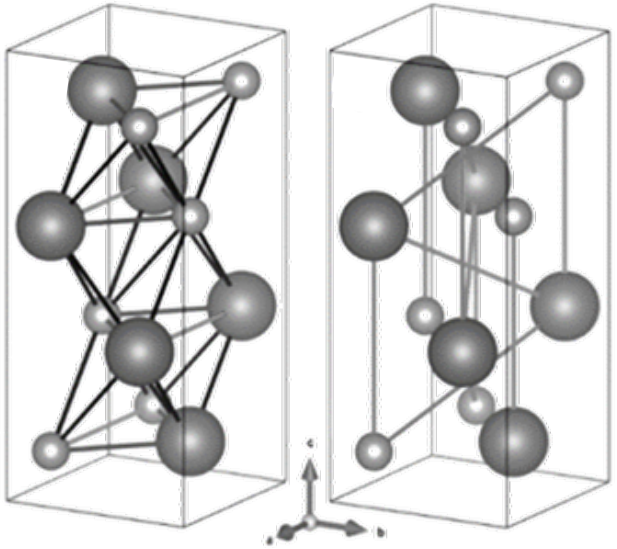

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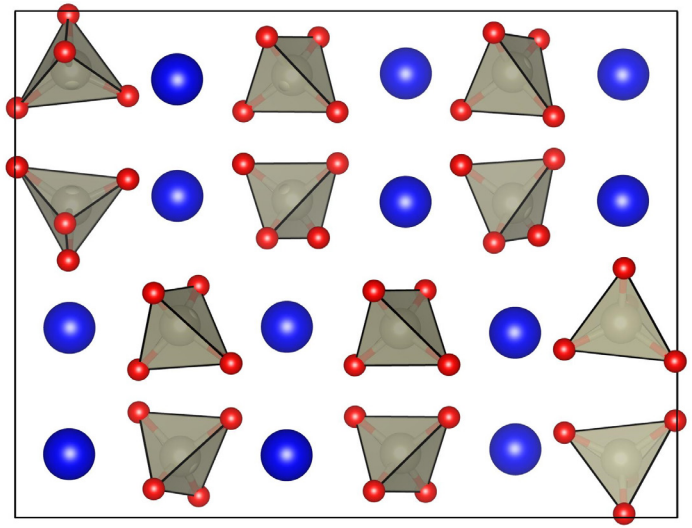

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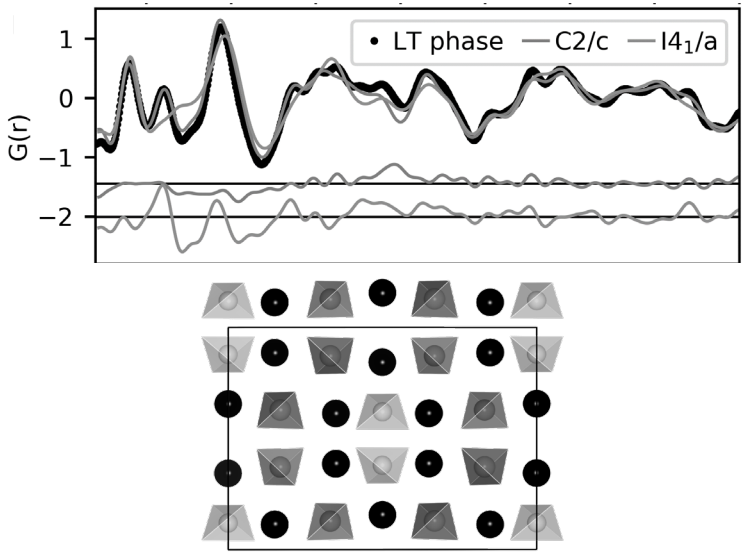

Structures with Post-Transition Metals

1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	* 71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	** 103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og
		* 57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb		
		** 89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No		

Variable Temperature Study of $TlReO_4$

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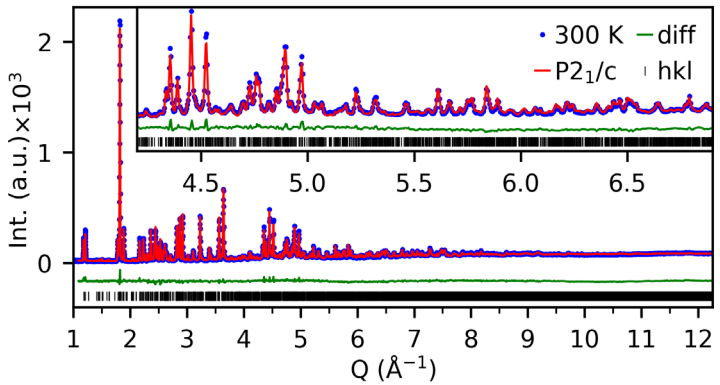
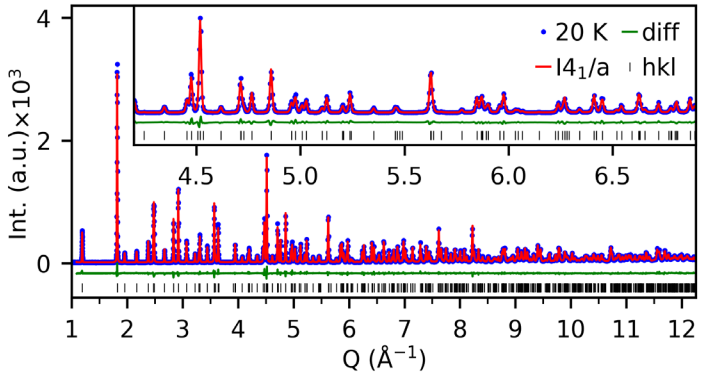
OAK RIDGE National Laboratory

Long-Range (POWGEN)

Monoclinic $P2_1/c$



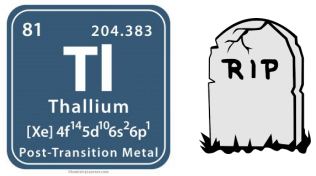
Tetragonal $I4_1/a$



Temperature

Tetragonal $I4_1/a$	500 K	Monoclinic $P2_1/c$
Monoclinic $P2_1/c$	300 K	Monoclinic $P2_1/c$
Tetragonal $I4_1/a$	20 K	Monoclinic $P2_1/c$

Short-Range (NOMAD)



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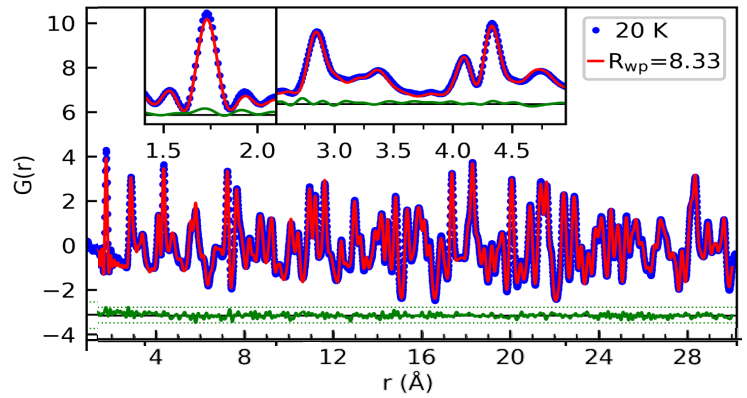

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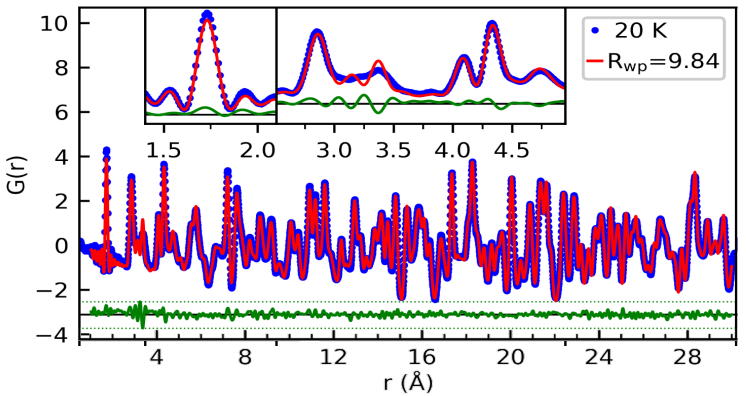
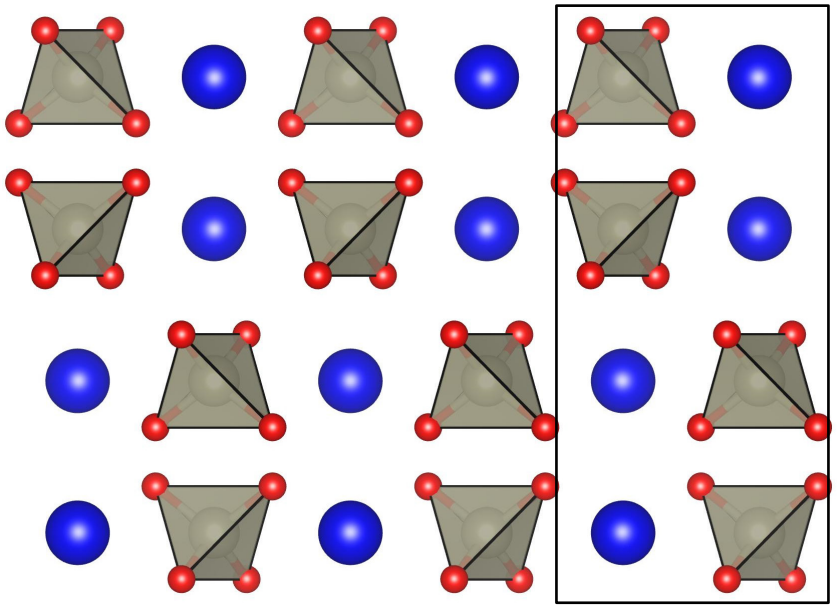
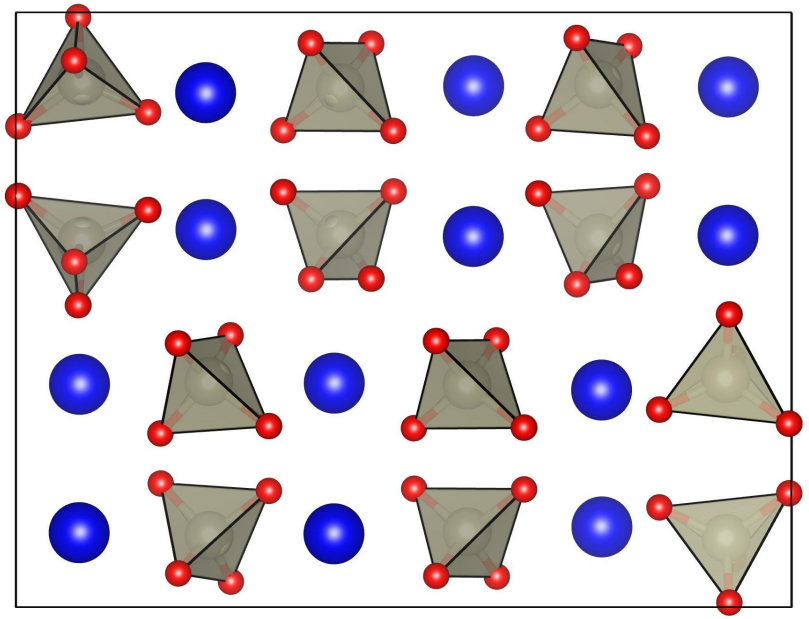
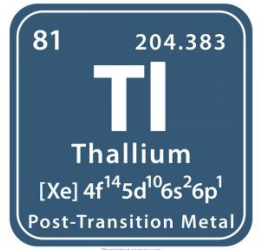


Saura Muzquiz, Mullens *et al.*; *J. Am. Chem. Soc.*, **2022**, *144* (34), 15612-15621.

The Hidden Structure of $TlReO_4$

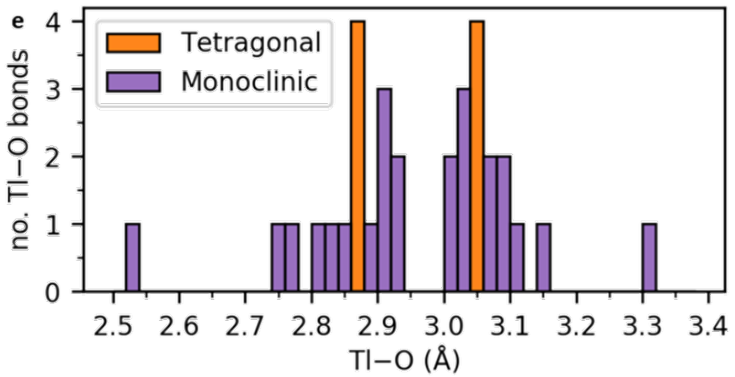






Tetragonal Long-Range
I*4$_1$/*a

Monoclinic Short-Range
P*2$_1$/*c



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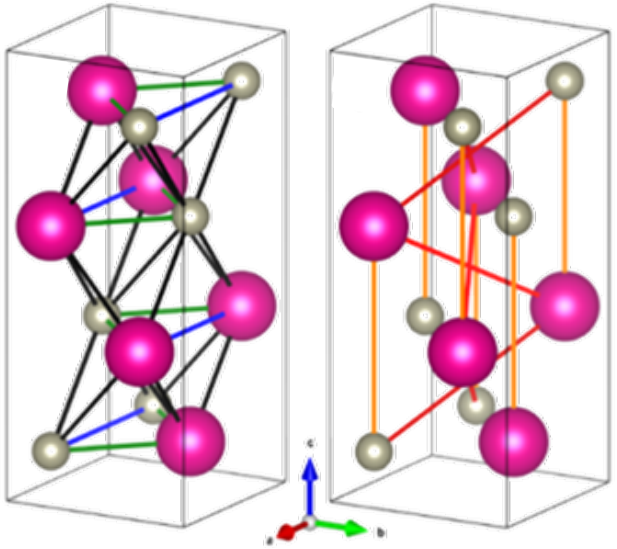

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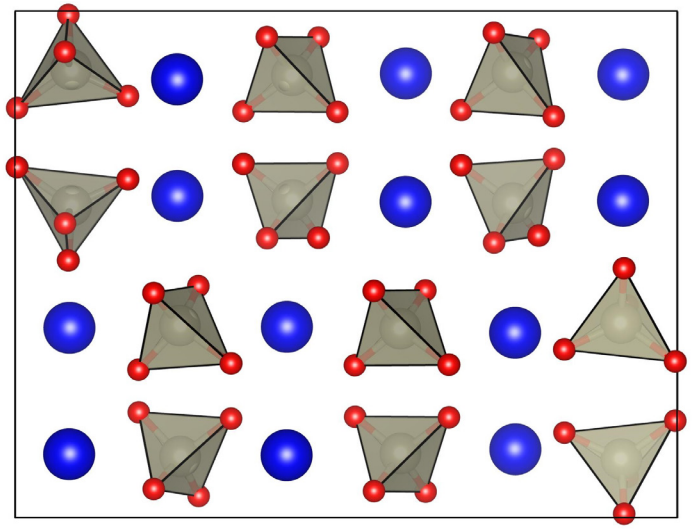

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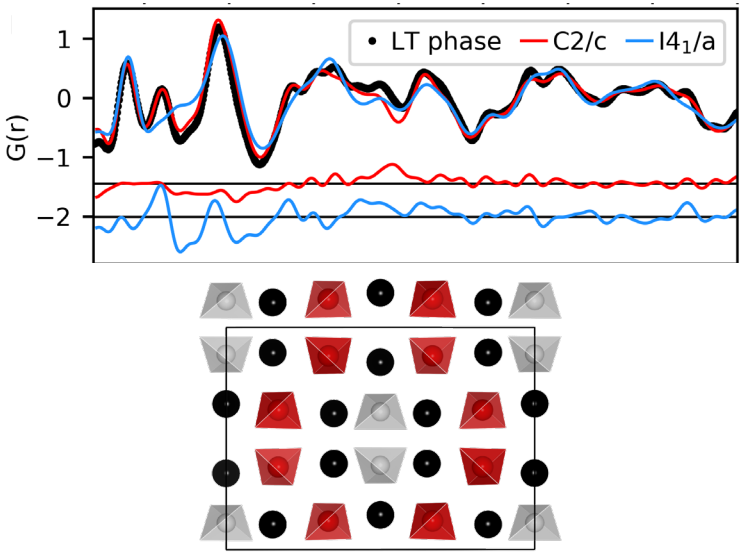

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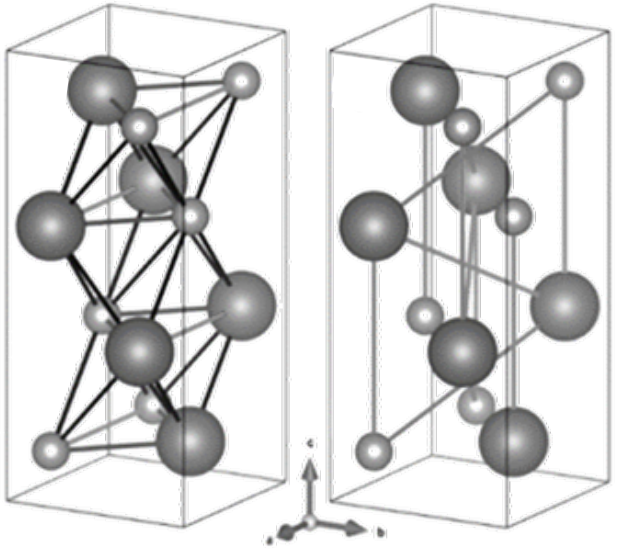

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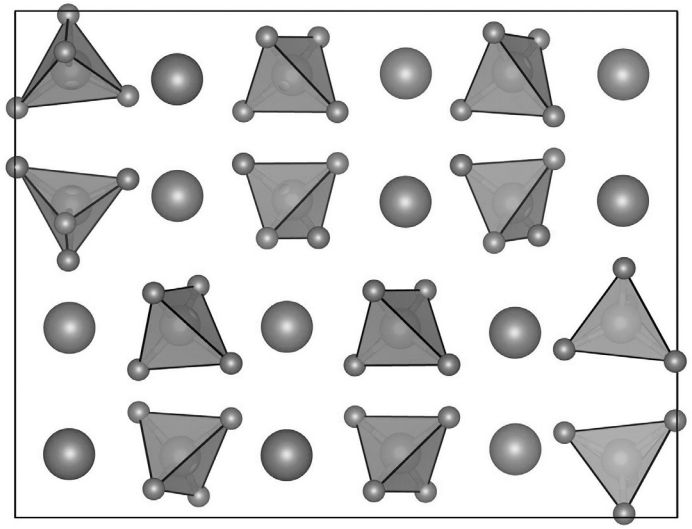

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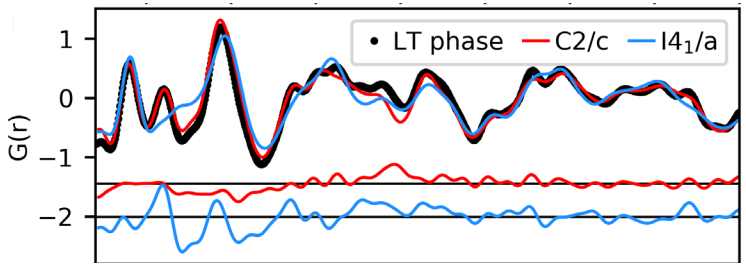
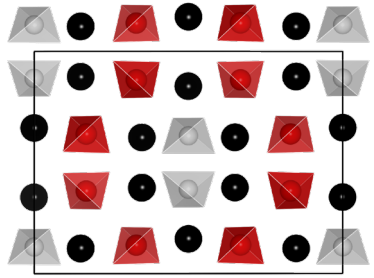
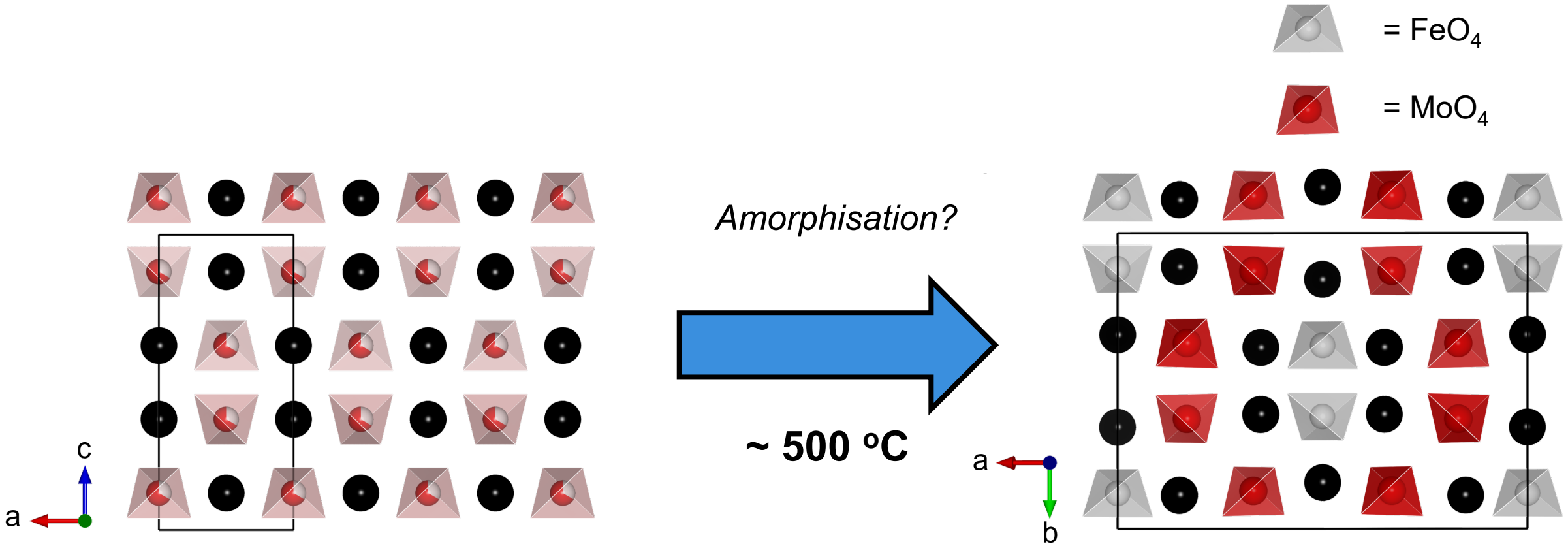




Phase Transformation in $Bi_3FeMo_2O_{12}$

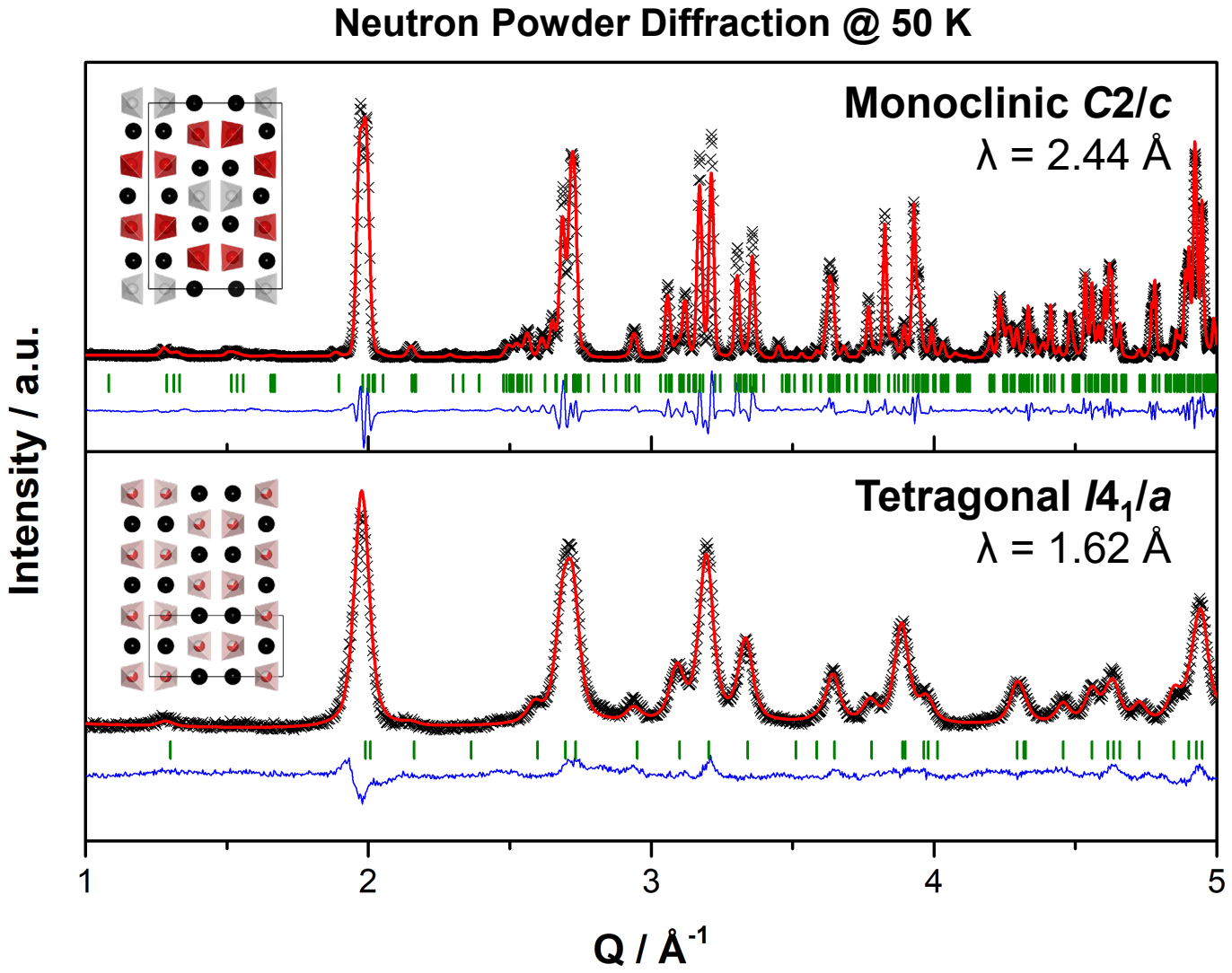


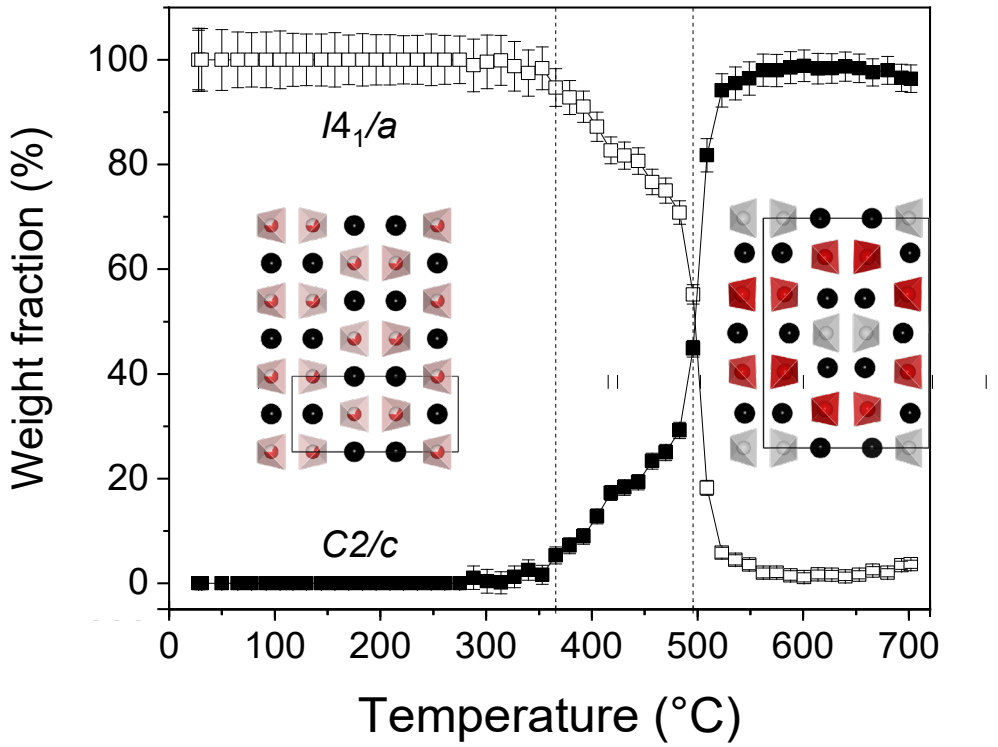
*I*4$_1$/*a*
Disordered Tetragonal Scheelite

*C*2/*c*
2:1 Ordered Monoclinic Fergusonite

Saura Muzquiz, Mullens *et al.*; *Unpublished*.

Variable Temperature Neutron Powder Diffraction





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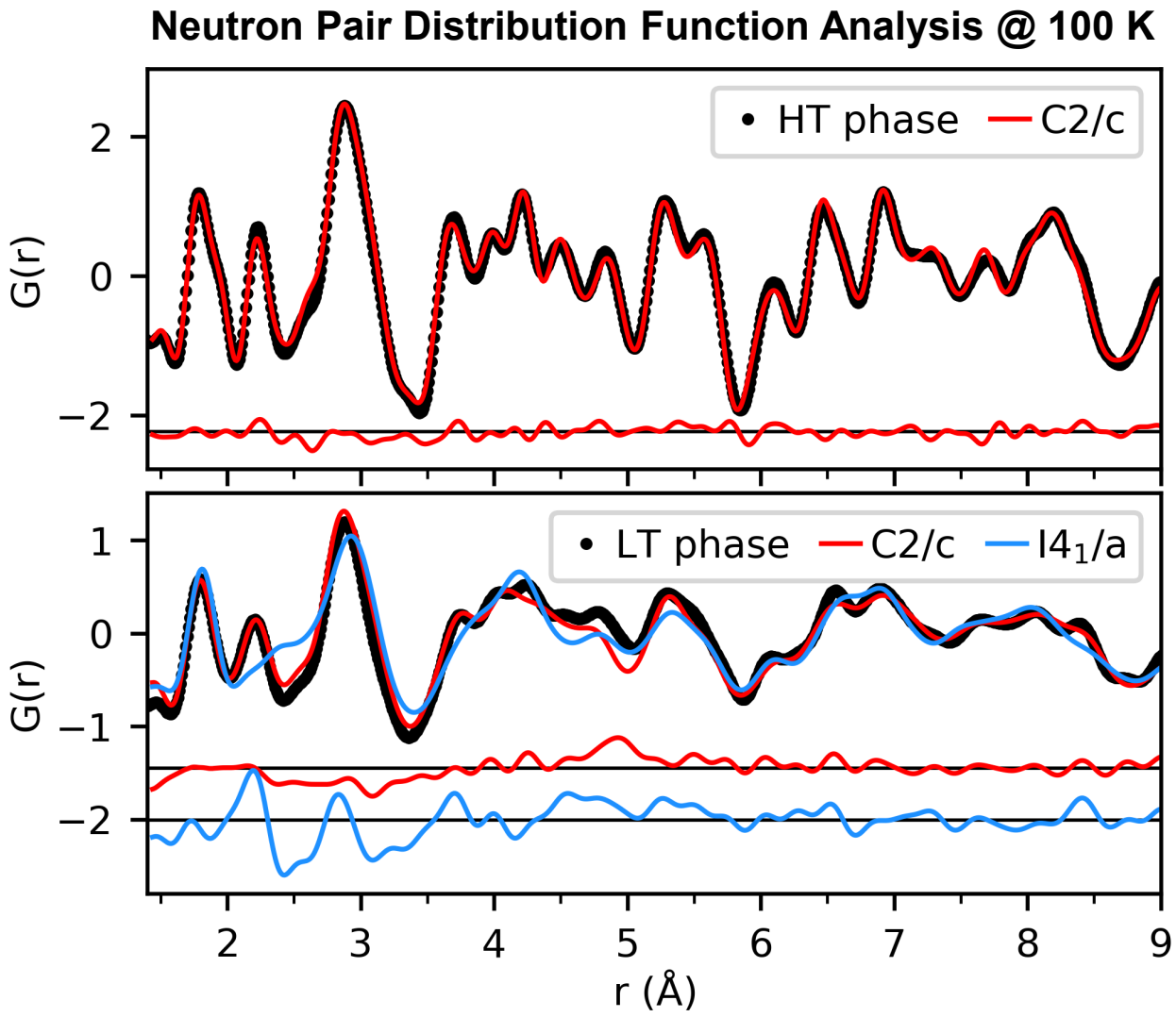

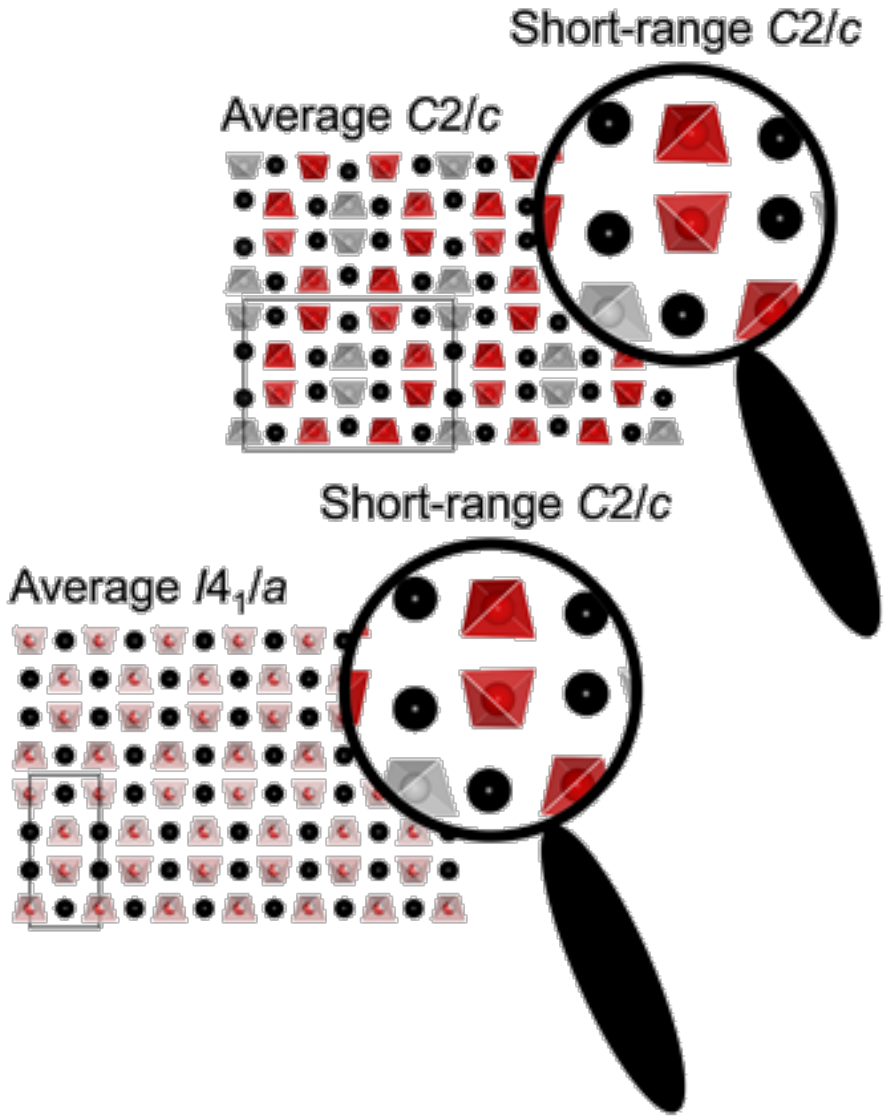

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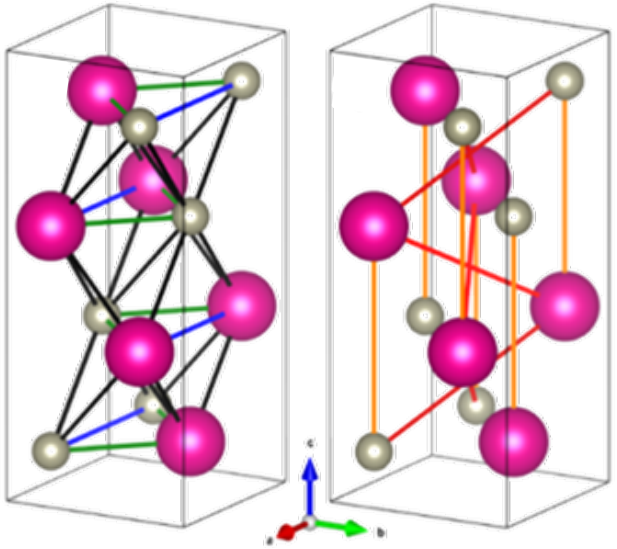

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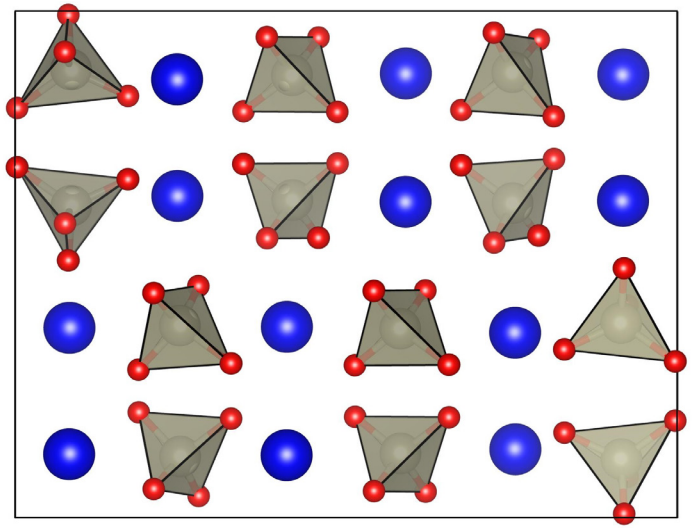

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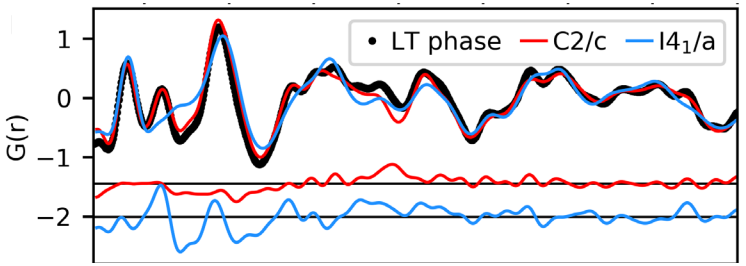
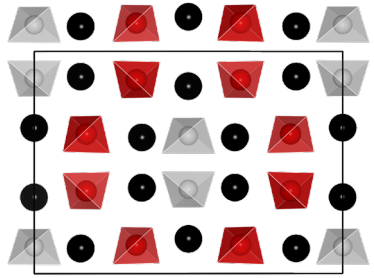
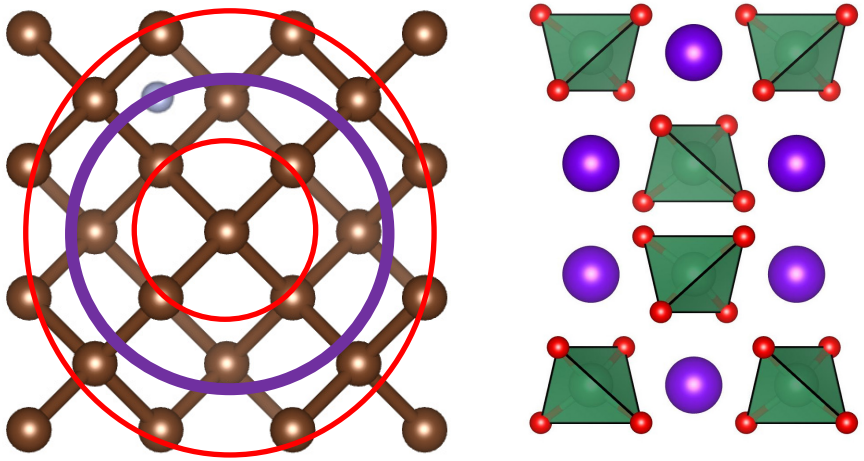
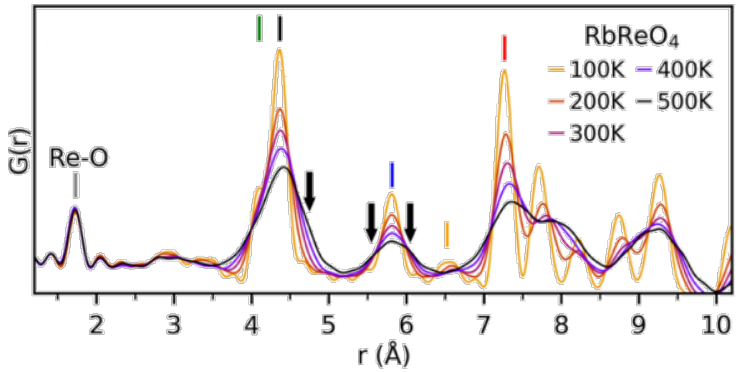


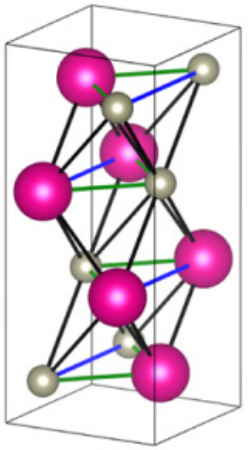


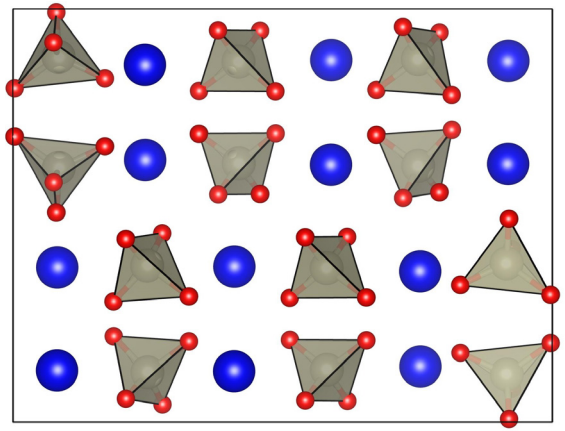
Difference in tetrahedra environments.

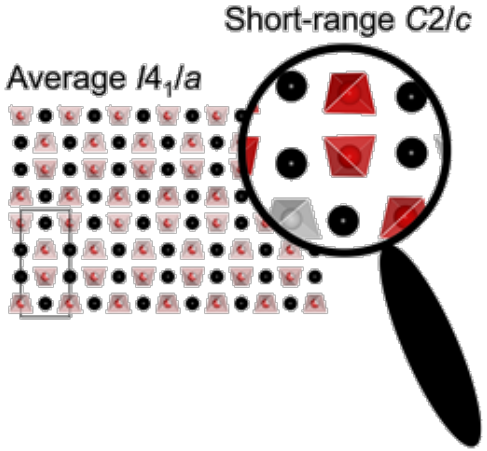
Conclusions

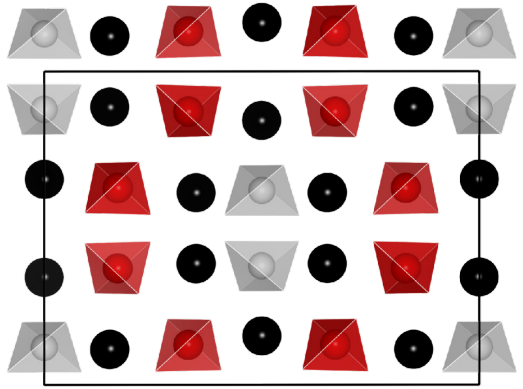












Email: bmul2806@uni.sydney.edu.au

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