

Average and Local Structure of $\text{NaCe}(\text{WO}_4)_2$ Nanophosphor: Structure-Property Correlation



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Plan of the talk

1. Introduction
2. Synthesis and Experimental studies
3. Structural characterization of $\text{NaCe}(\text{WO}_4)_2$
 - a) Average structure
 - b) Local Structure
4. Summary

Introduction



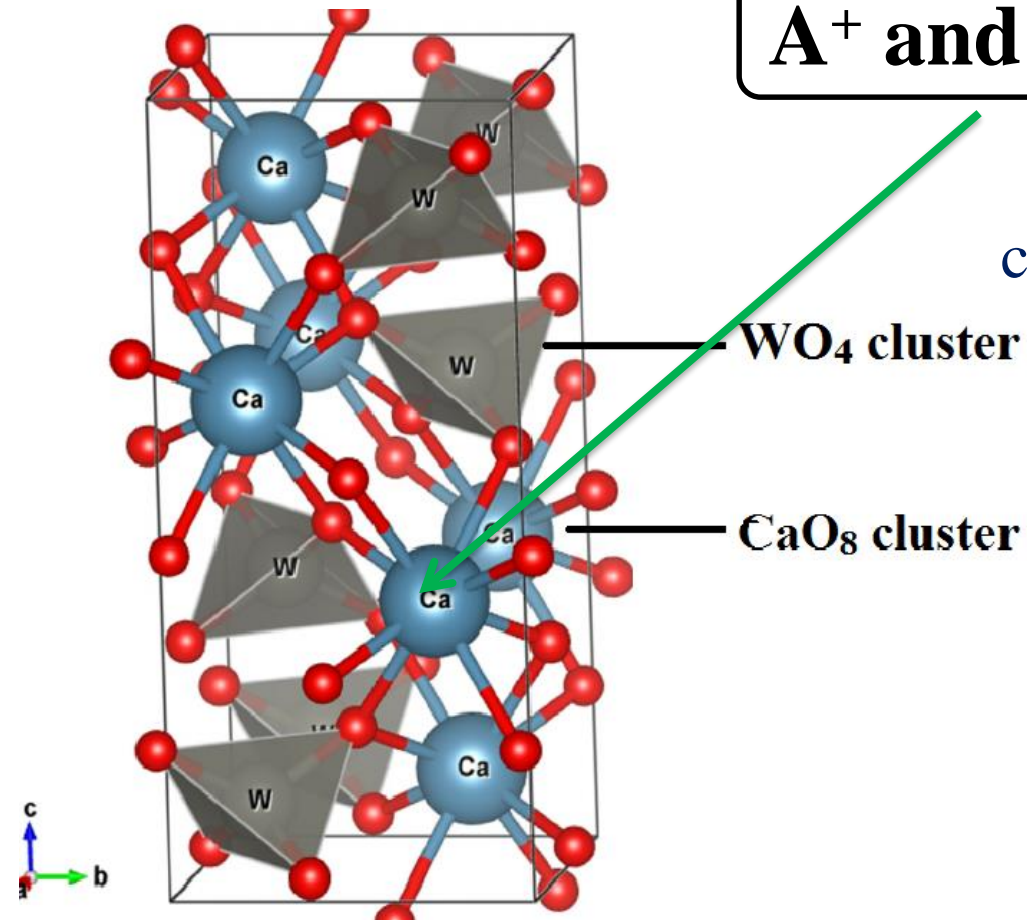
where A=Alkali metal ion and RE= TM (In/Y/Rareearths)



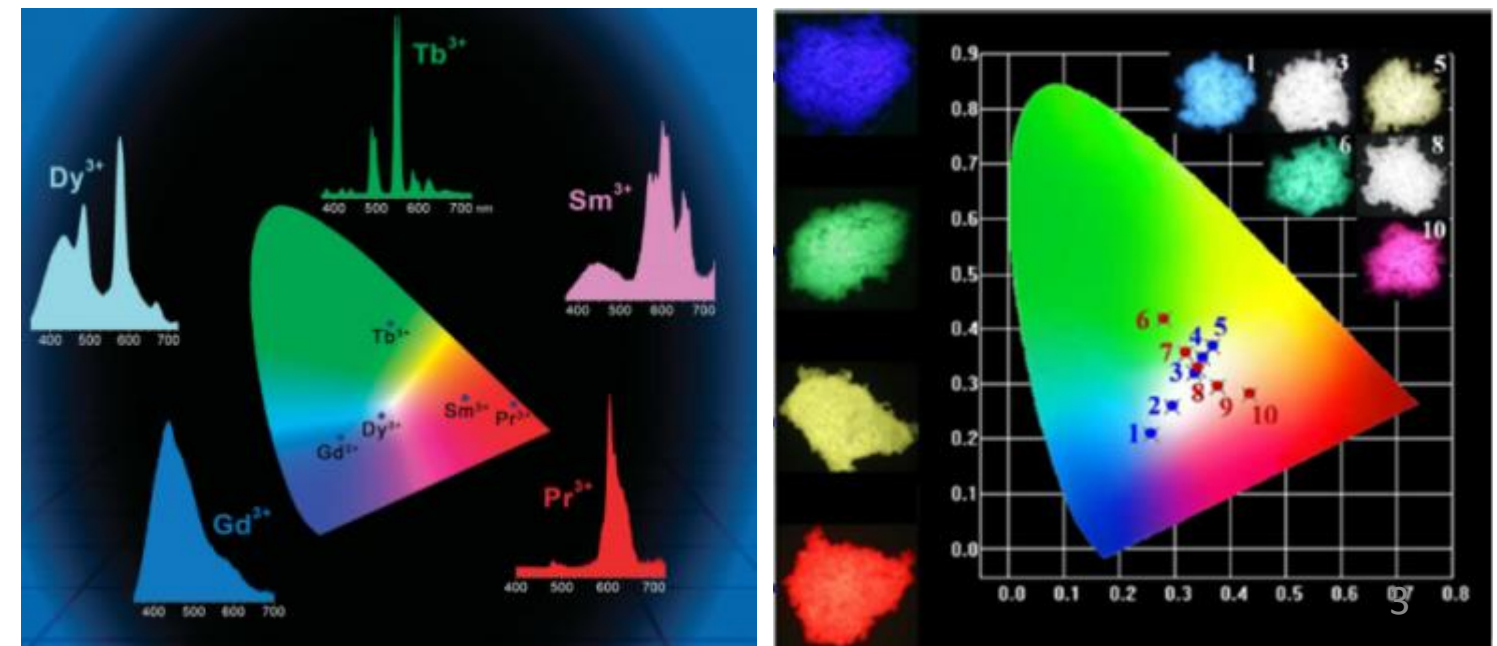
Shares same
crystallographic site

1. Structural distortion
2. Lowering of symmetry
3. Phase transition

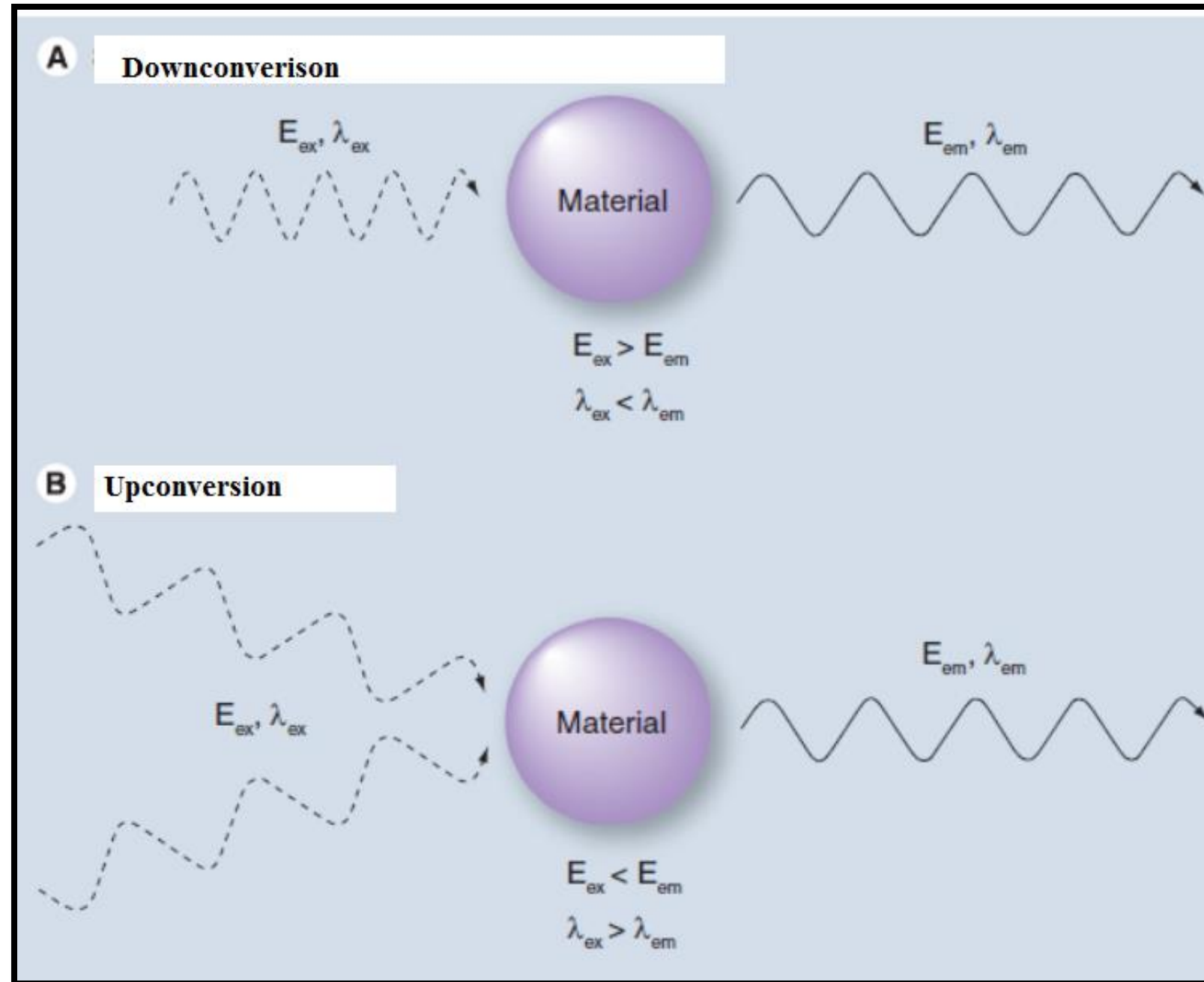
Optical properties



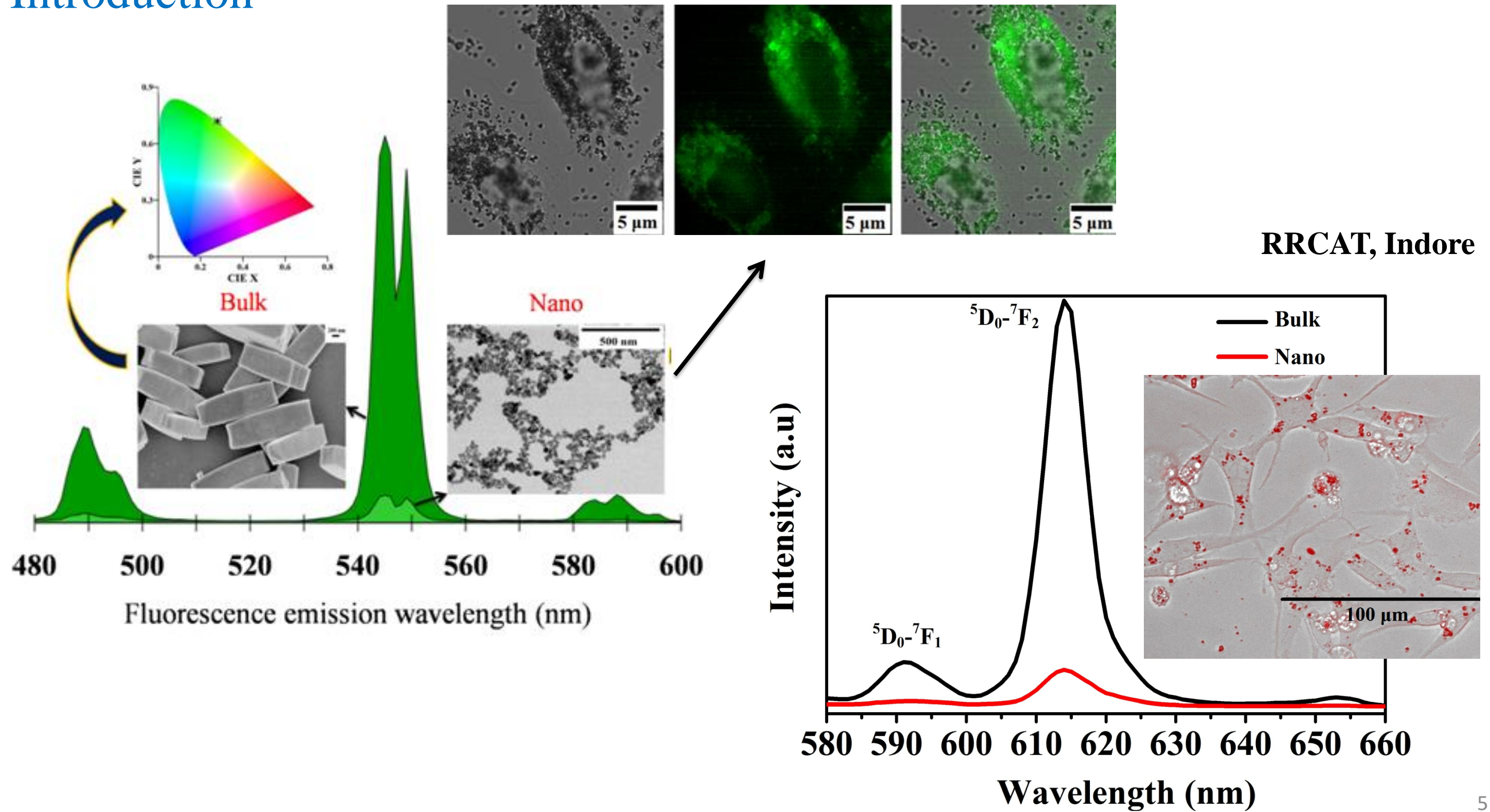
CaWO₄ Scheelite structure



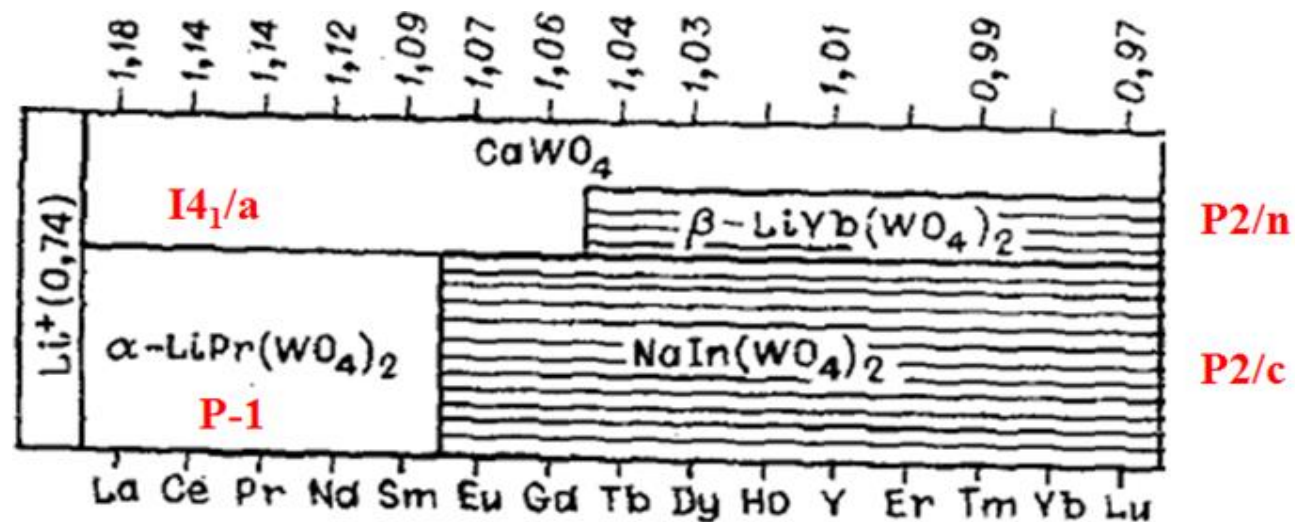
Introduction



Introduction



RRCAT, Indore



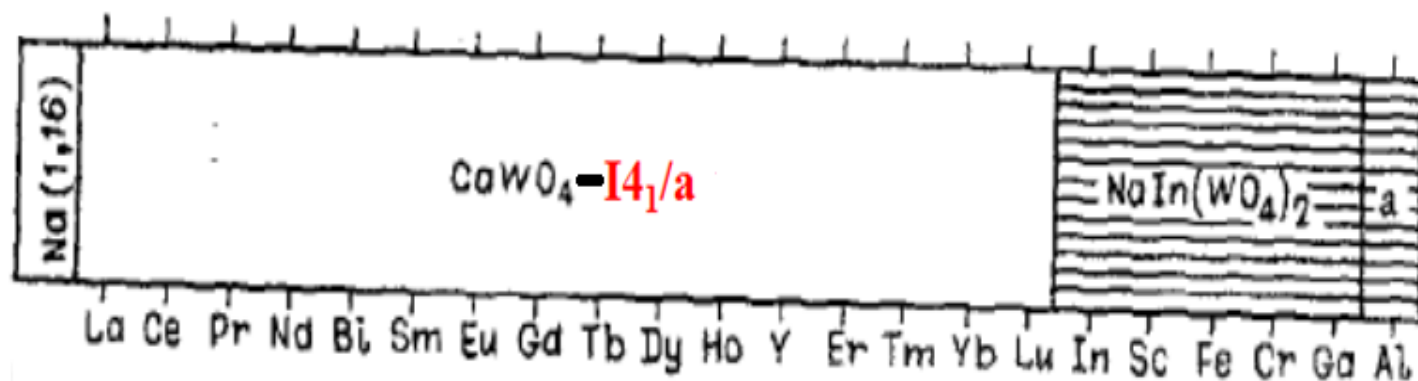
THE JOURNAL OF PHYSICAL CHEMISTRY C

J. Phys. Chem.: A B C Letters Pre-1997

Article

In Situ Neutron Diffraction Studies of $LiCe(WO_4)_2$ Polymorphs: Phase Transition and Structure-Property Correlation

Archana K. Munirathnappa^{1†}, Debasmita Dwivedi^{§1}, James Hester[‡], Prabeer Barpanda[§], Diptikanta Swain[‡], Chandrabhas Narayana[#], and Nalini G. Sundaram^{*†‡}



Synthesis-Solvothermal method-Tunable parameters

Stoichiometric amount of all precursors

Dissolved in MilliQ water

Precursor solution was mixed slowly

Transferred to Teflon lined stainless steel autoclave

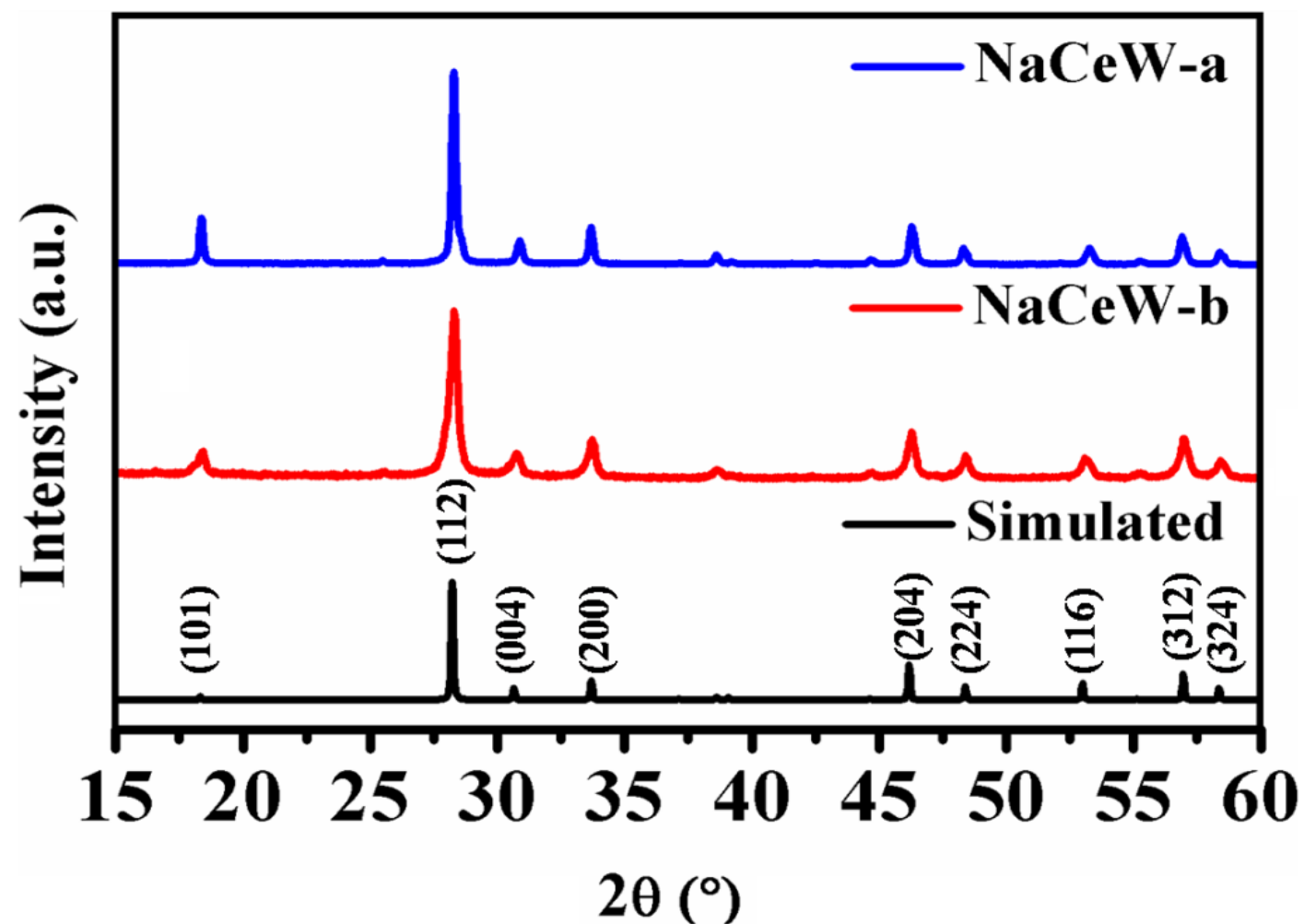


Final product

NaCeW-a (water)
NaCeW-b (Ethylene Glycol)

200 °C and 30hr

Effect of solvent on phase formation and crystallinity

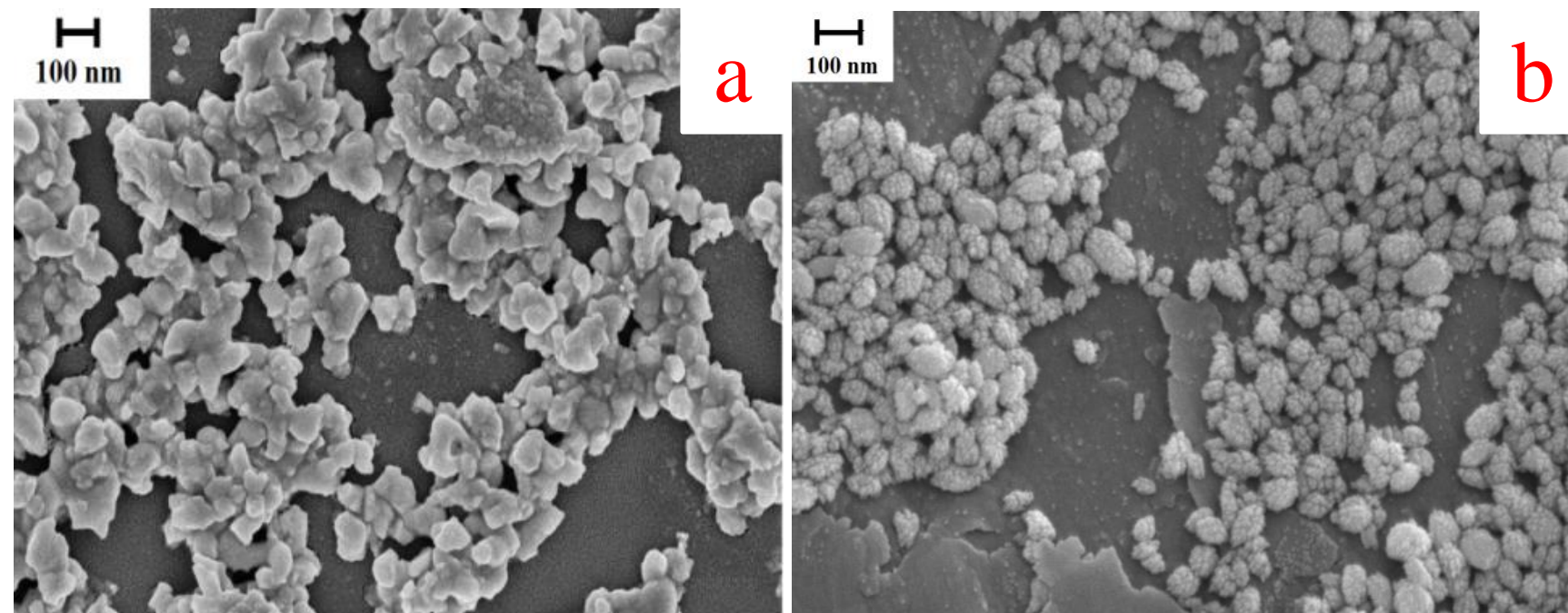


Name of the Material	Crystallite size (nm)	Lattice strain (10^{-3})
NaCeW-a	80.7	3.6
NaCeW-a	41.5	6.0

Broadened peaks in NaCeW-b suggests the formation of smaller crystallite size in ethylene glycol compared to water

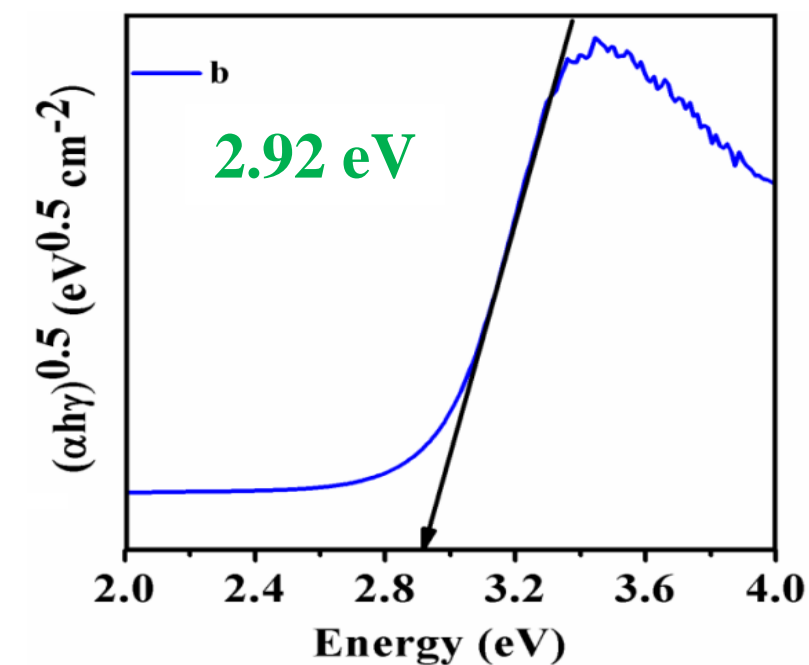
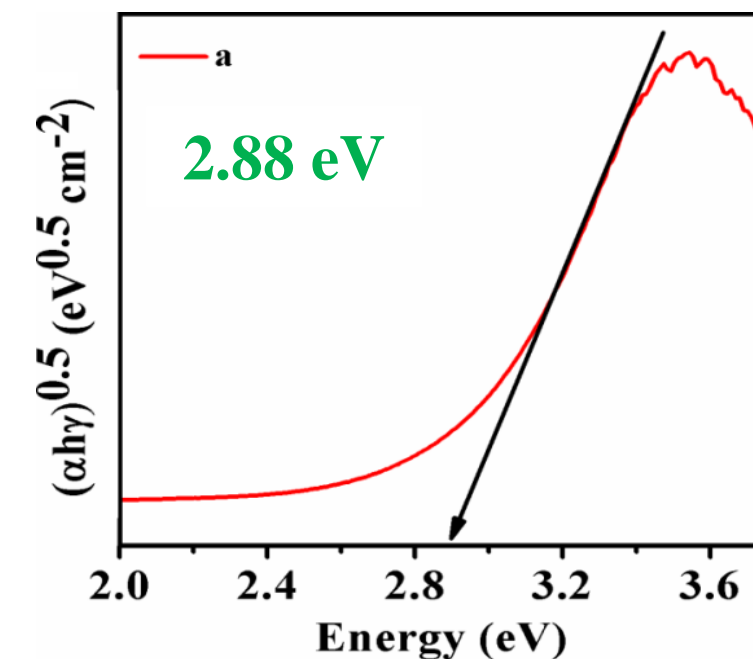
Powder XRD patterns

Microscopy and UV-Diffuse Reflectance Studies



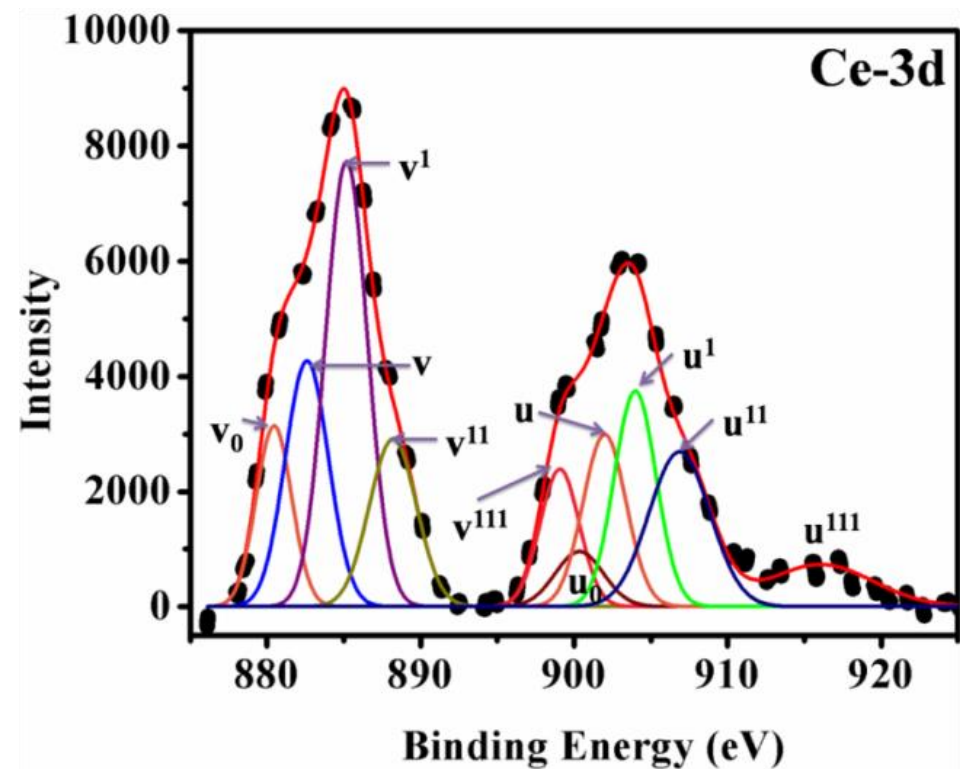
a) Irregular sized agglomerated particles of smooth morphology and particle size in the range 150-200 nm

b) Homogenous Berry like morphology (80-100 nm)



Tauc plots of obtained from the diffuse reflectance spectra using Kubelka-Munk function

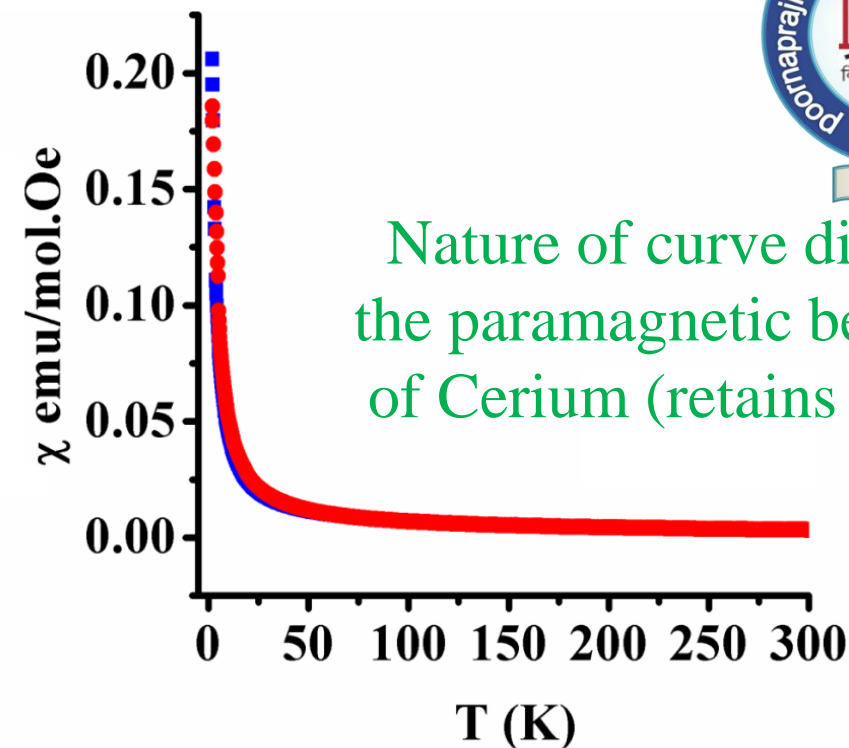
X-ray Photon Spectroscopy and Magnetic studies



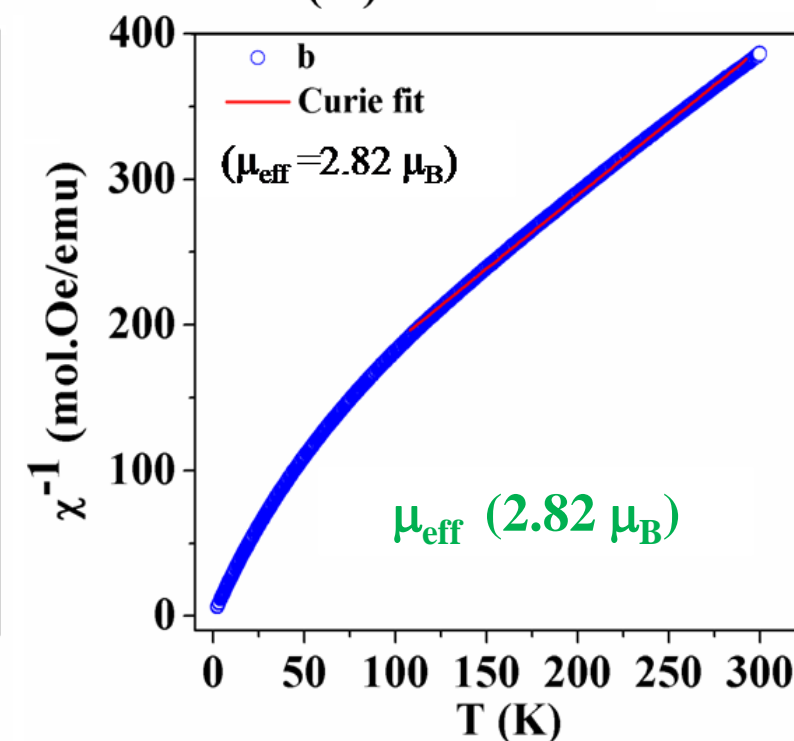
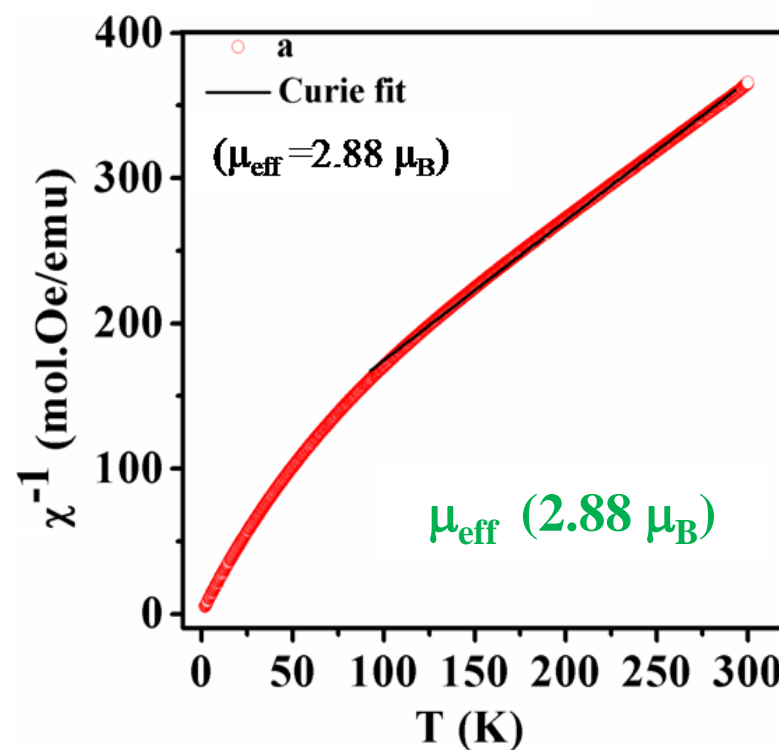
High resolution XPS spectrum of Ce-3d with the corresponding deconvoluted peaks.

Confirms the presence of +3 valence state of cerium ion

Temperature dependent magnetic susceptibility (χ) against temperature

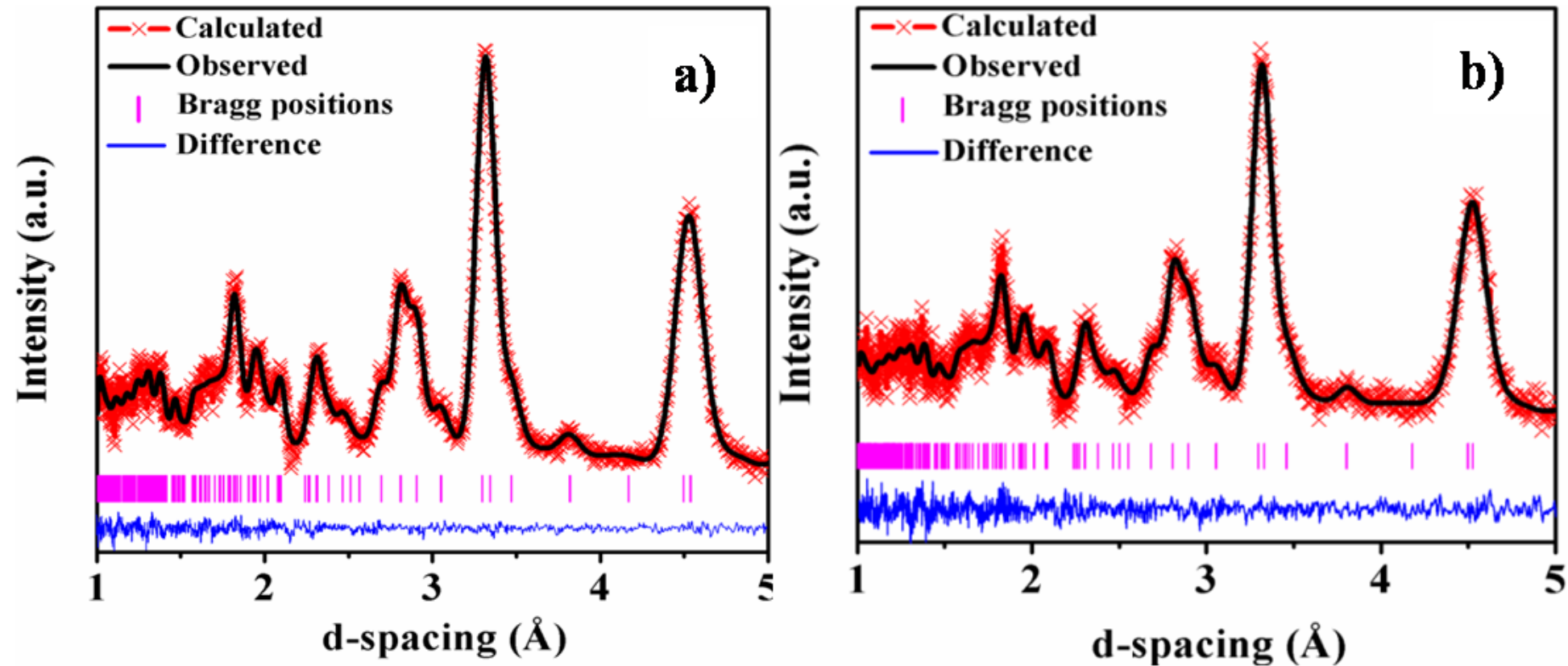


Nature of curve dictates the paramagnetic behavior of Cerium (retains its +3)



Inverse magnetic susceptibility (χ^{-1}) against temperature

Crystal structure analysis studies via Rietveld refinements method using neutron diffraction data collected on NOMAD instrument, ORNL US.



Rietveld refined patterns of $\text{NaCe}(\text{WO}_4)_2$ synthesized by solvothermal method
a) NaCeW-a and b) NaCeW-b

$\text{Na}_{0.5}\text{Ce}_{0.5}\text{MoO}_4$ as standard model (ICSD No 67493) crystallizing in $I4_1/a$

Crystallographic data of $\text{NaCe}(\text{WO}_4)_2$ obtained from Rietveld refinements using NPD data

Crystallographic data	NaCeW-a	NaCeW-b
$a=b$ (Å)	5.332 (2)	5.334 (2)
c (Å)	11.677 (2)	11.681 (2)
$\alpha=\beta=\gamma$ (°)	90	90
Unit cell volume (Å ³)	332.06 (2)	332.37 (2)

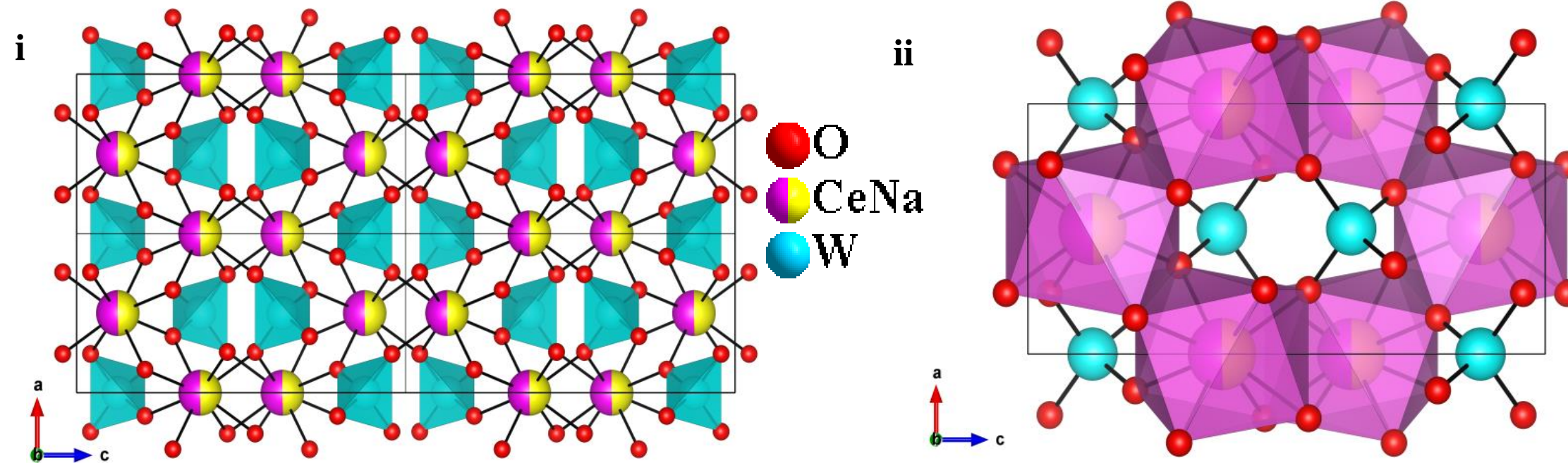
Material	NaCeW-a	NaCeW-b
RWp (%)	5.0	4.4
Rp (%)	4.1	3.4
RI_(cal) (%)	6.5	6.7

Atomic coordinates, occupancies and isotropic thermal parameters

Sample	Oxygen positions			Occupancy				U_{iso} (Å ²)		
	x	y	z	Na	Ce	W	O	Na/Ce	W	O
NaCeW-a	0.1434 (1)	0.0103 (2)	0.2020 (2)	0.5	0.5	1.0	1.0	0.014 (2)	0.007 (2)	0.029 (1)
NaCeW-b	0.1473 (1)	0.0108 (2)	0.2083 (2)	0.5	0.5	1.0	1.0	0.006 (2)	0.007 (1)	0.014 (1)

Na and Ce at (0.0, 0.75, 0.875) and W at (0.5, 0.75, 0.125) (special positions)

Average crystal structure representation and unit cell representation of NaCeW along *b*-direction



- ✓ Na and Ce shares same crystallographic site
- ✓ Tungsten forms regular WO_4 (tetrahedra) and cerium forms CeO_8 polyhedra
- ✓ WO_4 and CeO_8 are connected by single oxygen atom

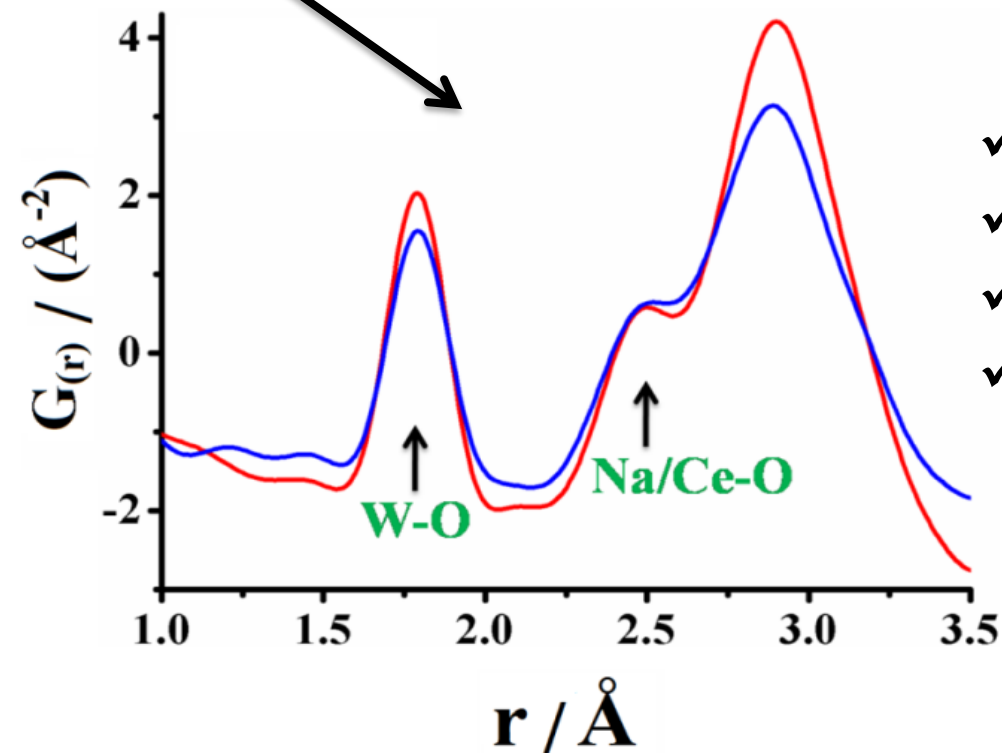
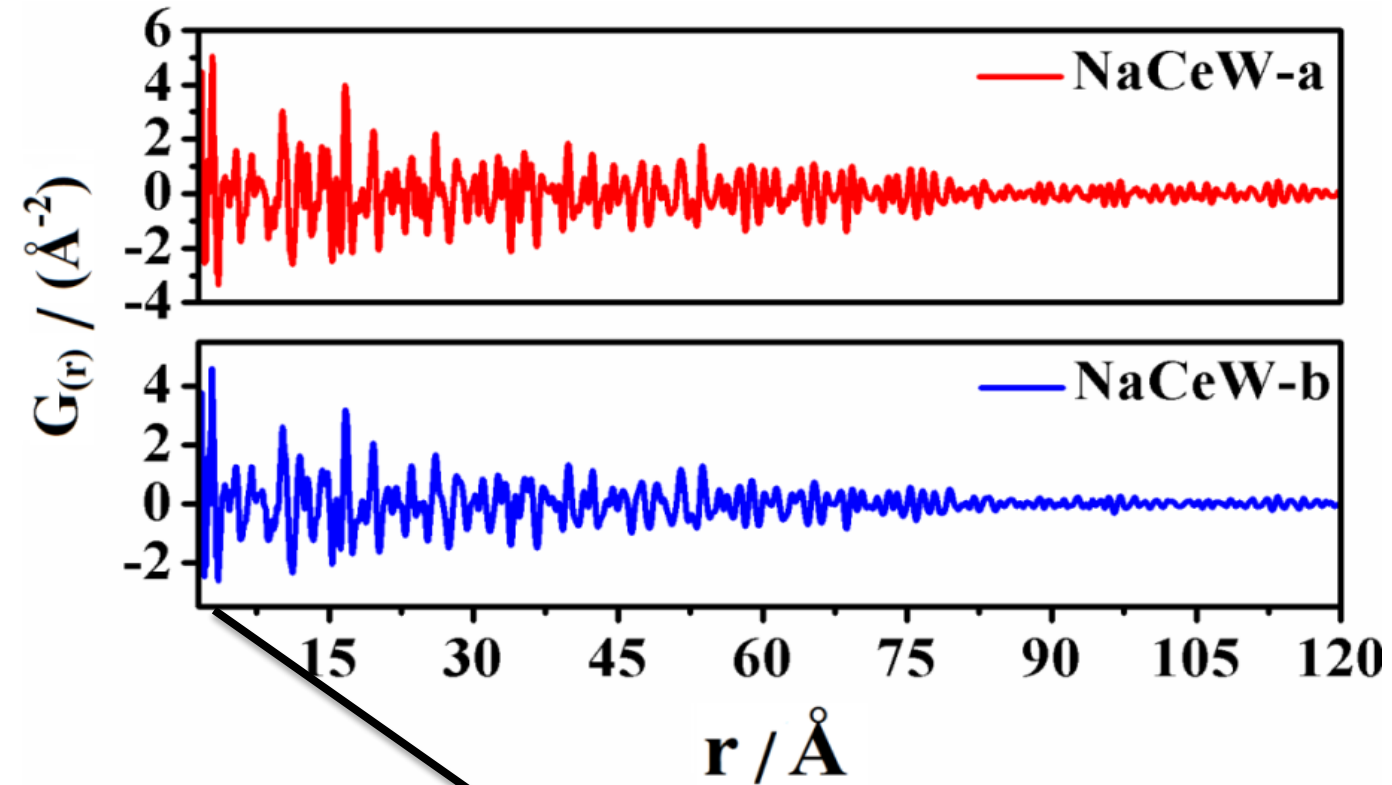
<i>Bond type</i>	<i>CN</i>	<i>Bond length (Å)</i>	
		<i>NaCeW-a</i>	<i>NaCeW-b</i>
Na/Ce-O	4	2.520 (2)	2.518 (2)
Ce/Na-O	4	2.567 (3)	2.535 (3)
W-O	4	1.740 (2)	1.787 (2)

Local structure analysis via total scattering pair distribution function (PDF) method.

Real-space Rietveld

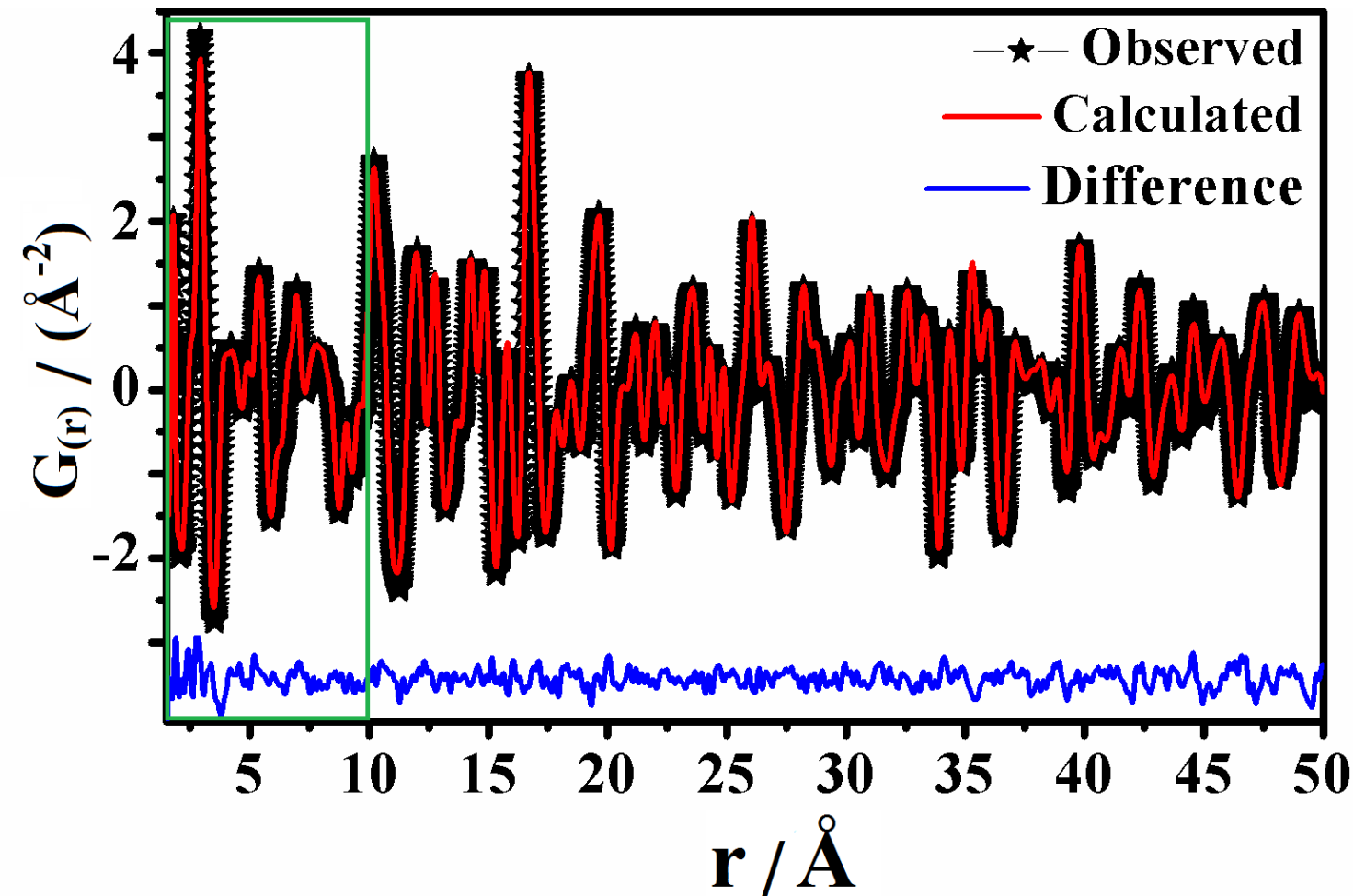
NOMAD, ORNL, US

$Q_{\max} = 31.41 \text{ \AA}^{-1}$
 295 K
 $r = 1.5 \text{ to } 50 \text{ \AA}$
 $Q_{\text{damp}} = 0.01765$
 $Q_{\text{broad}} = 0.01918$

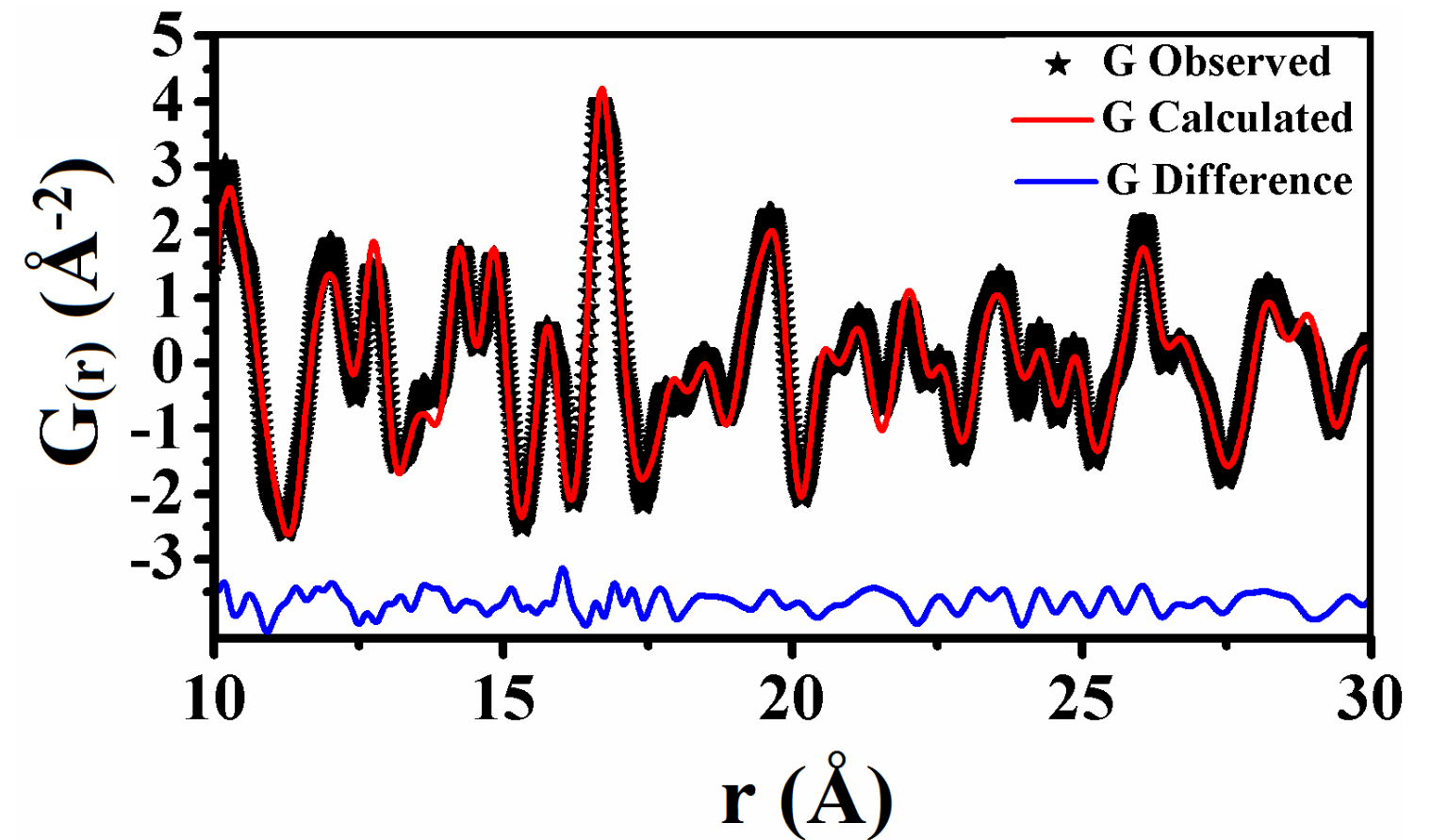


- ✓ Interatomic distances
- ✓ Bond lengths
- ✓ Level of disorder
- ✓ Coordination number

Centrosymmetric $I4_1/a$ model from Rietveld refinement

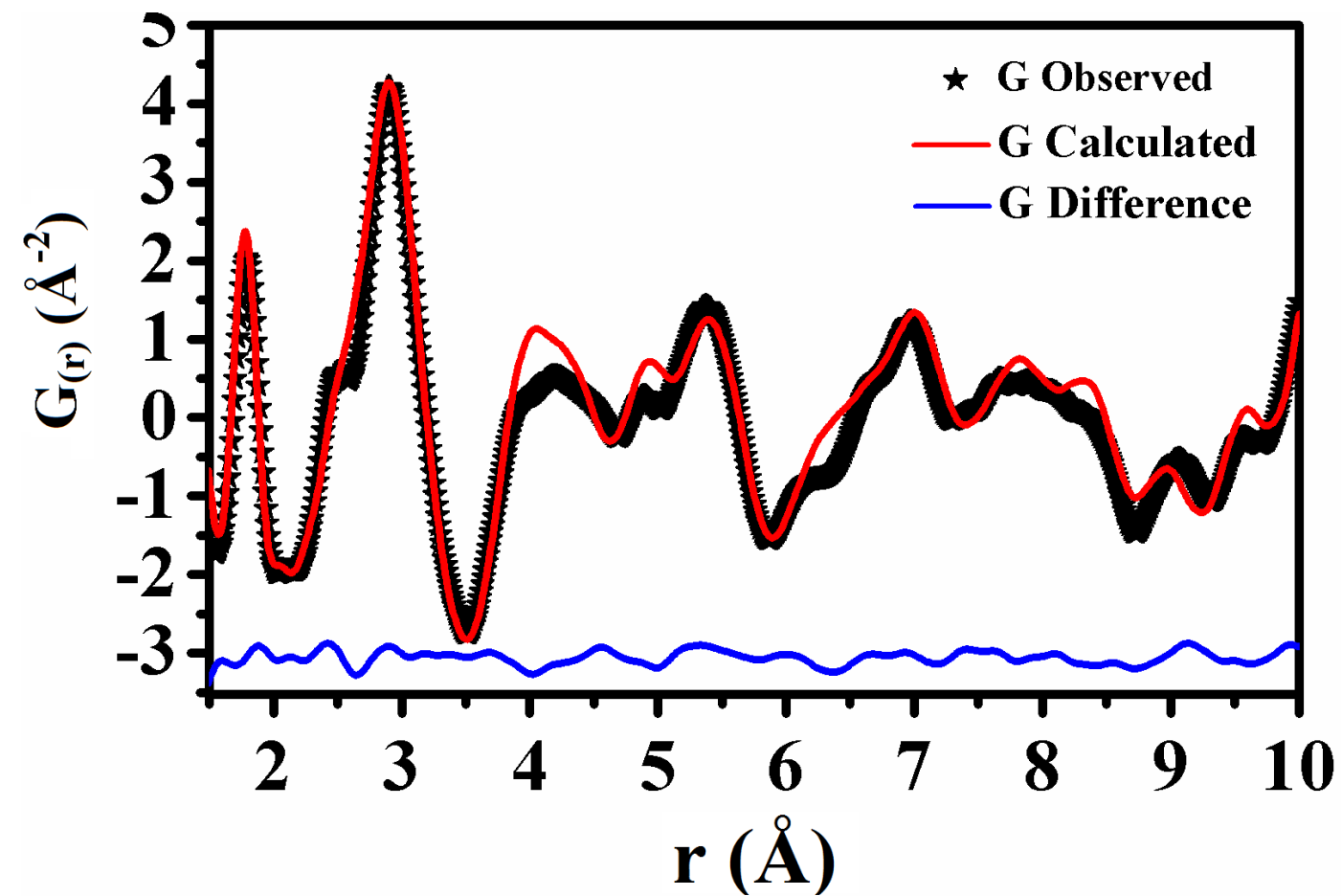


Long r-range

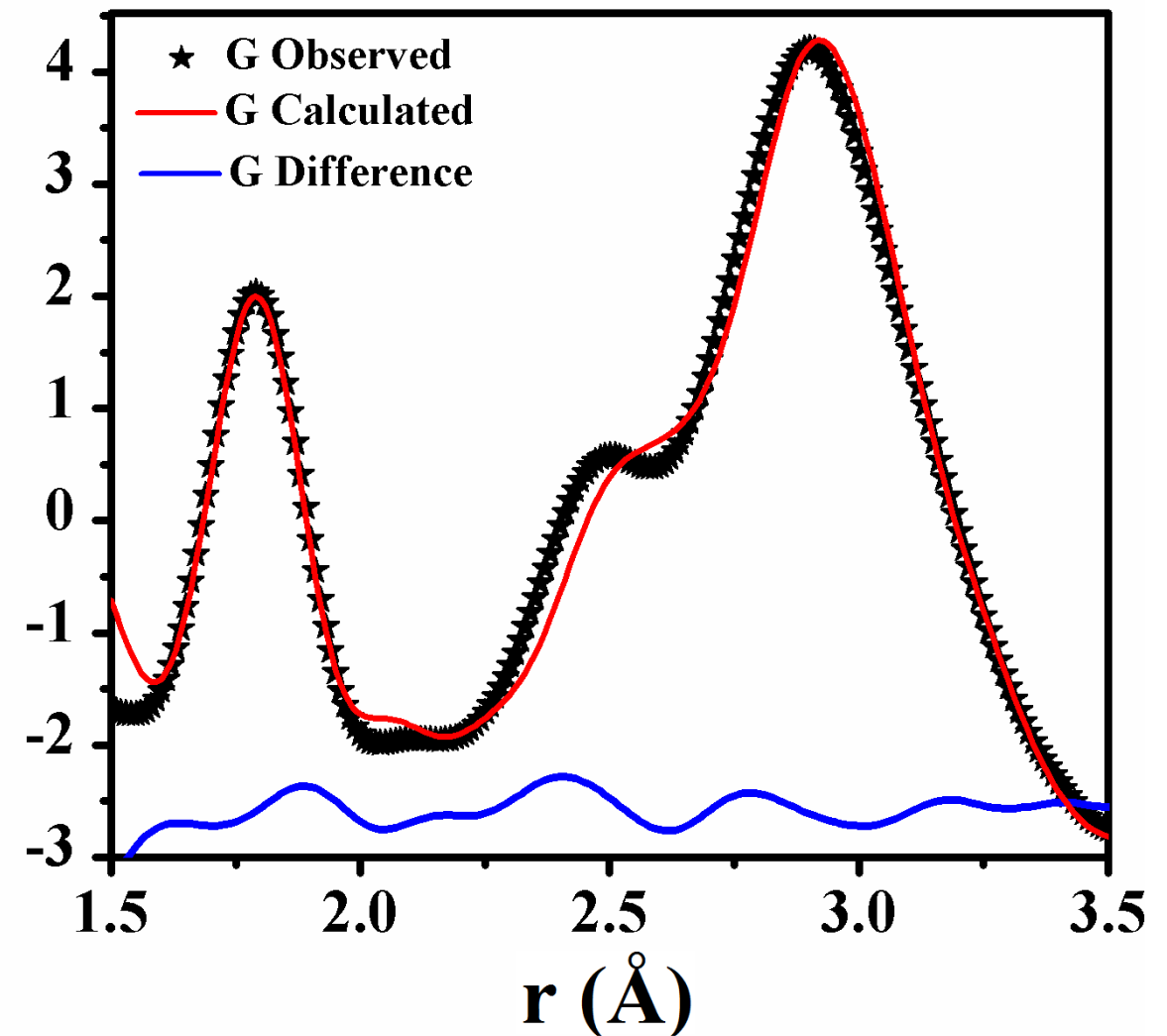


Observed (black), calculated (red) and difference PDF plot (blue) of NaCeW-a with $R_w = 9.9\%$. Green box indicates the region with relatively poor fit below 10 \AA .

PDF refinement in specific ranges using centrosymmetric $I4_1/a$ model from Rietveld refinement



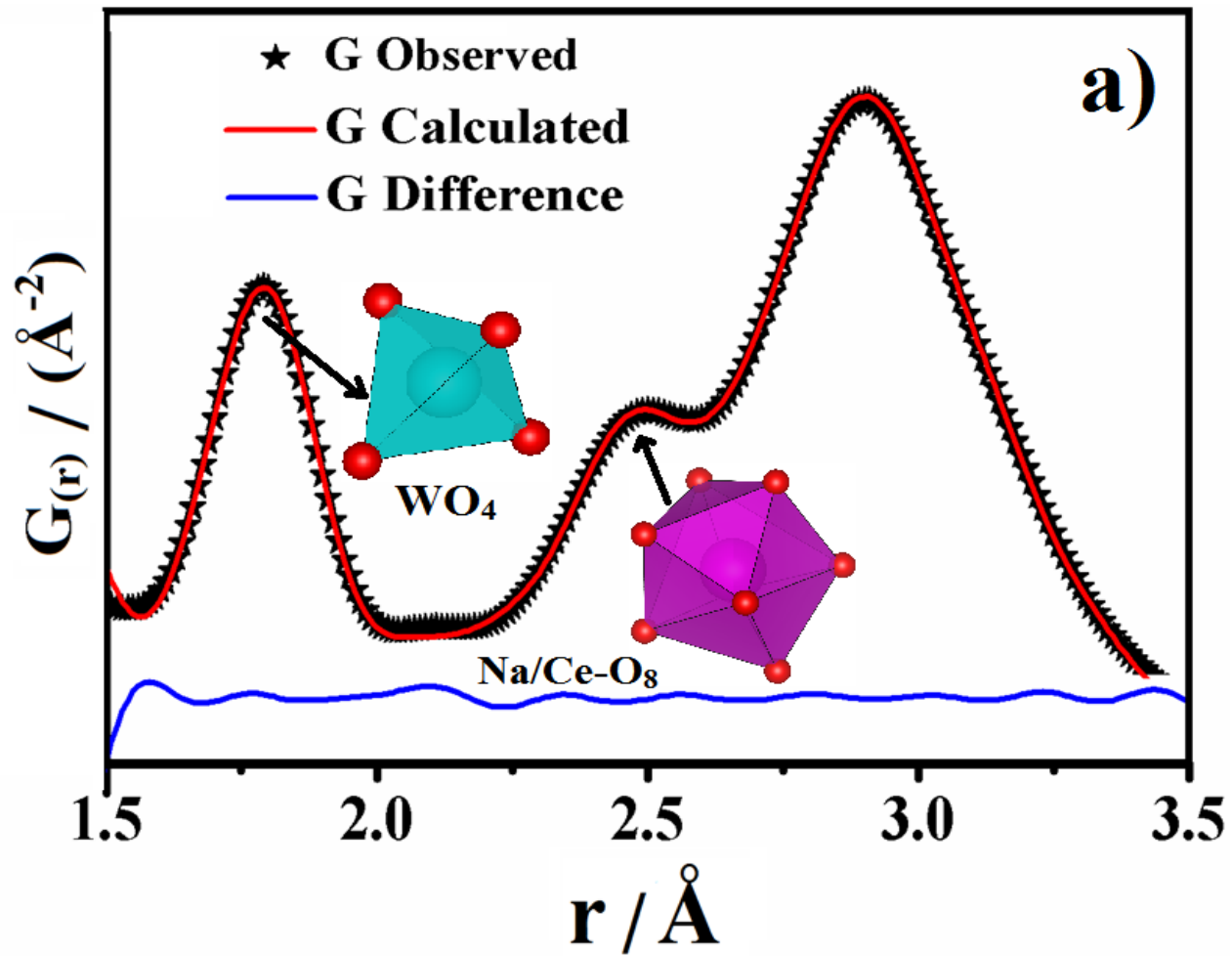
Medium r-range



Short r-range

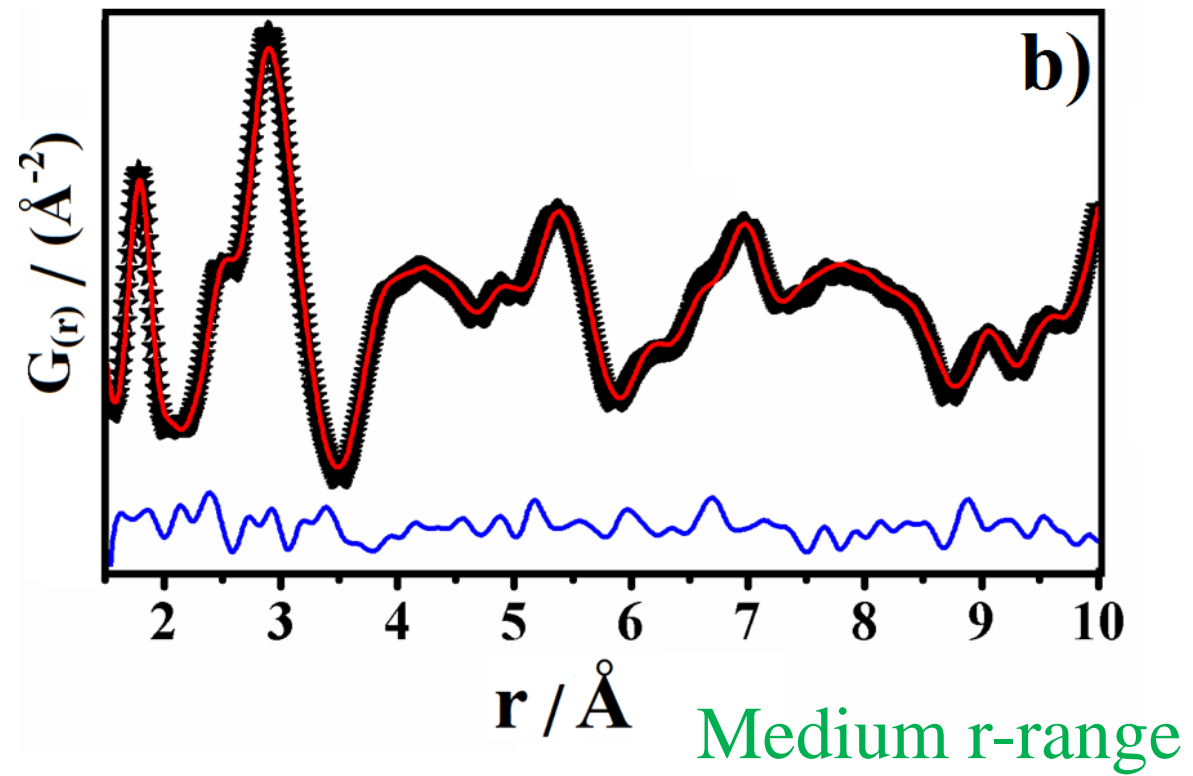
R_w (%)=11.7

Noncentrosymmetric ($I\bar{4}$ model)
 [LiYb(MoO₄)₂ (ICSD No: 152282)]

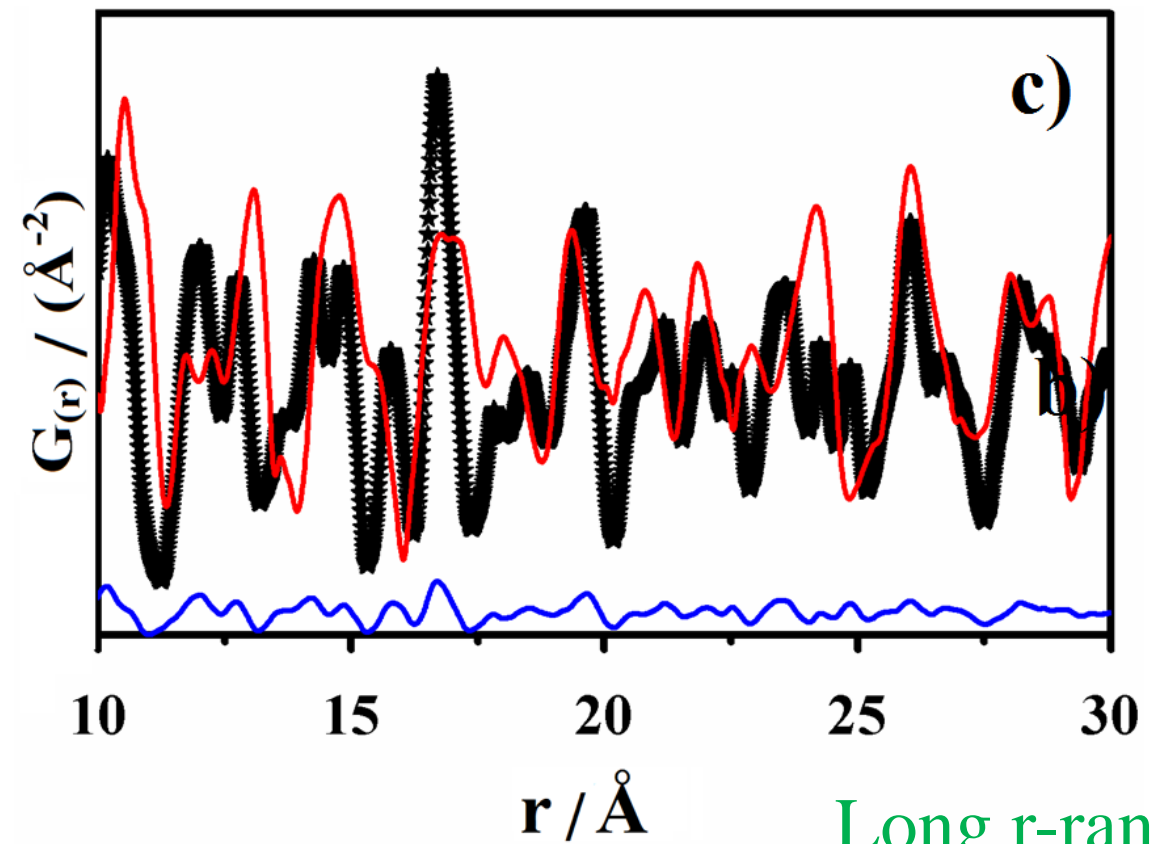


Short r-range

R_w (%) = 3.7

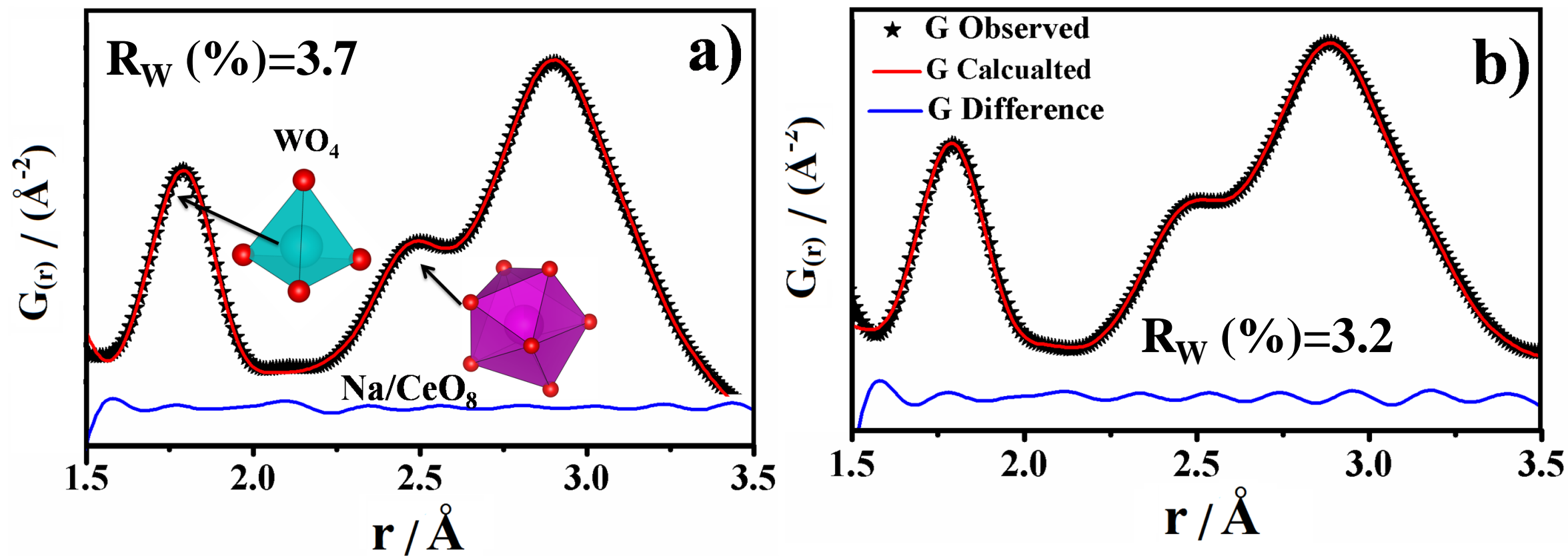


Medium r-range



Long r-range

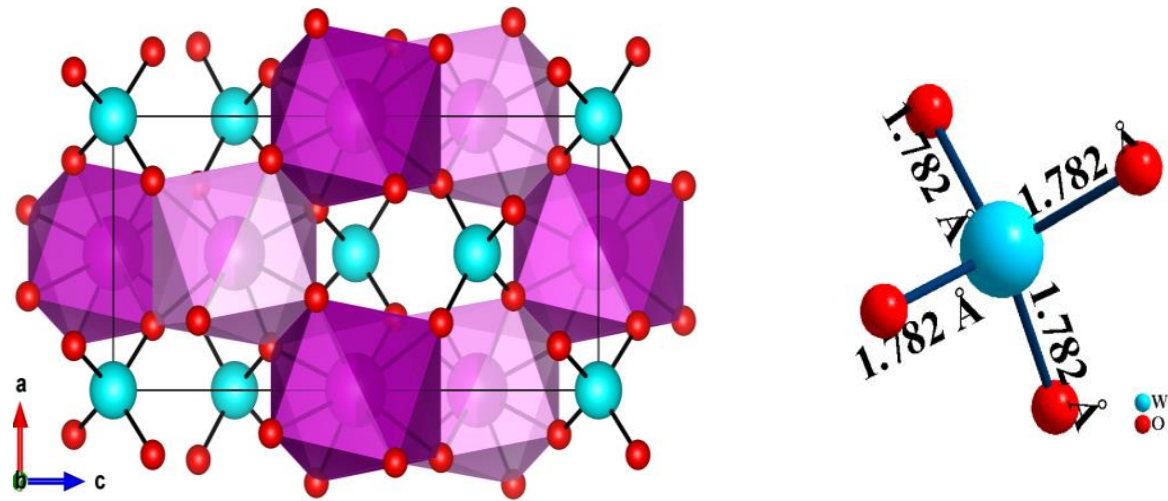
Noncentrosymmetric $I\bar{4}$ model



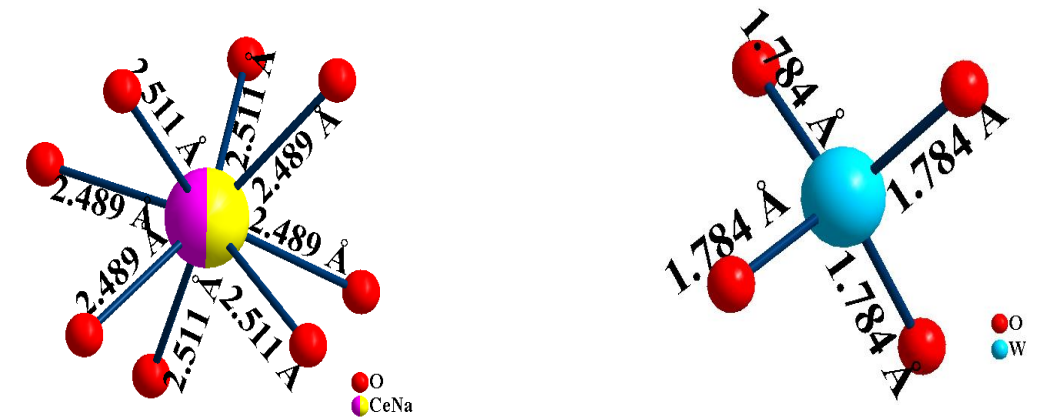
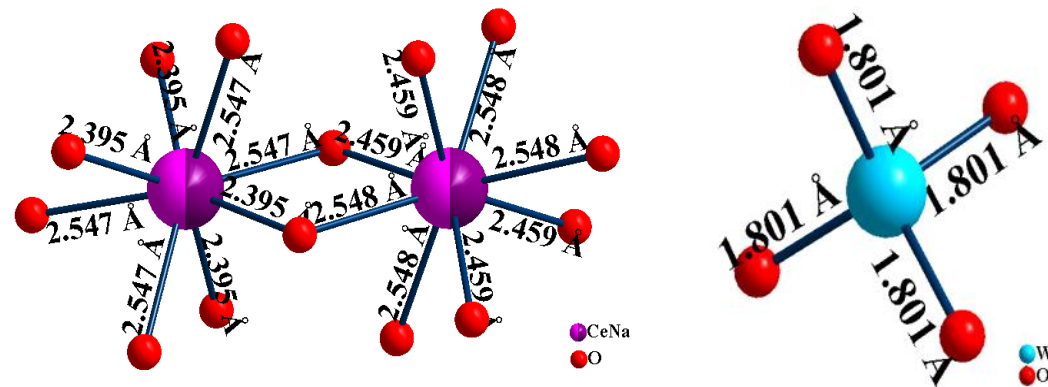
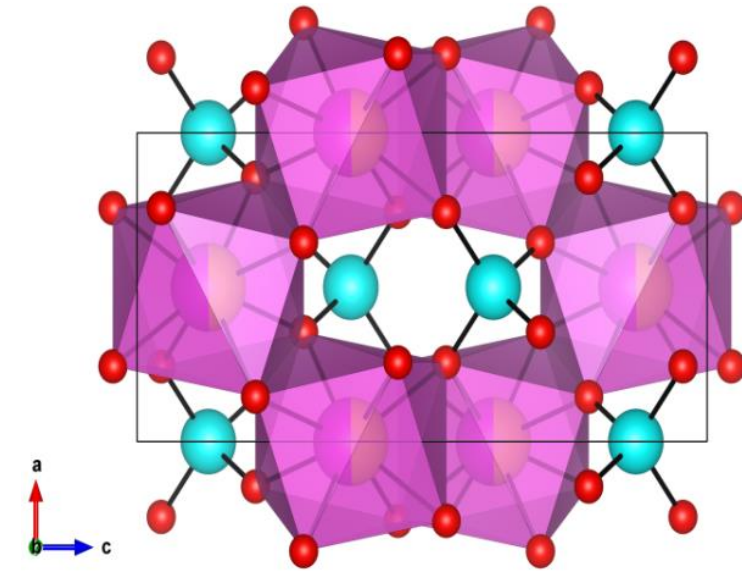
Observed (black), calculated (red) and difference PDF plot (blue)
of NaCeW-a and NaCeW-b

Structural variations in average and local structure of $\text{NaCe}(\text{WO}_4)_2$

Local structure $I\bar{4}$ space group
(non centrosymmetric)



Average structure $I4_1/a$ space group
(centrosymmetric)



Schematic representation of unit cell in average structure and local structure of NaCeW-a

Crystallographic data of NaCeW-a using $I\bar{4}$ model and $I4_1/a$ model
at r=1.5 to 3.5 Å obtained from PDF refinements.



Selected bond distances in NaCeW-a and NaCeW-b via PDF refinements from r=1.5 to 3.5 Å using $I\bar{4}$ model.

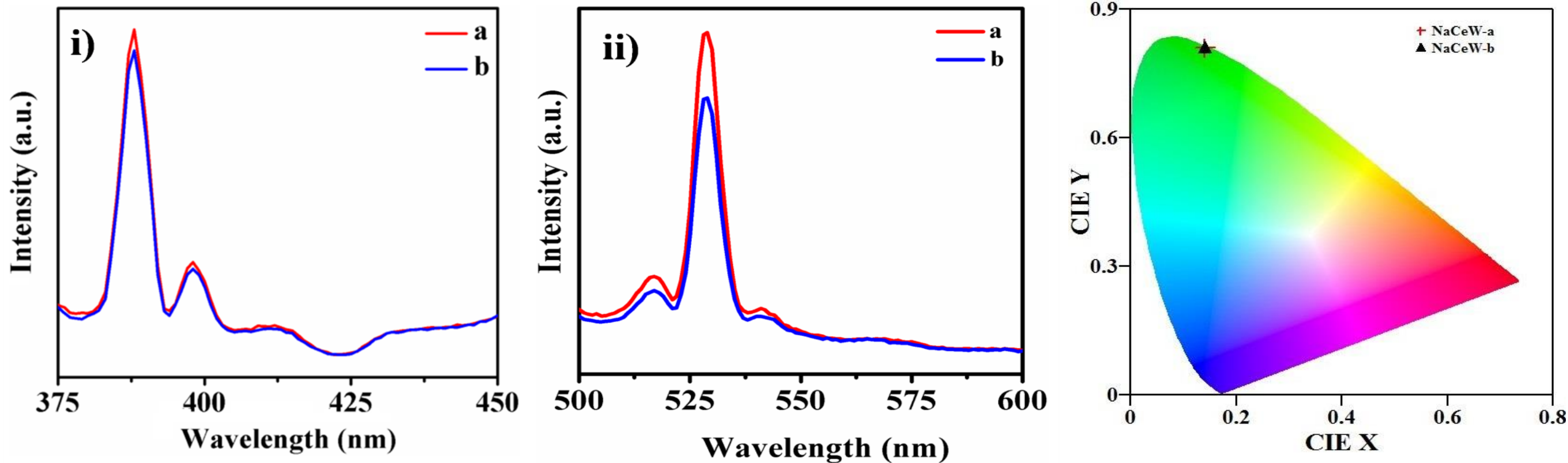
Crystallographic data Space group	NaCeW-a	
	a) $I\bar{4}$	b) $I4_1/a$
a=b (Å)	5.322 (2)	5.342 (1)
c (Å)	11.364 (2)	11.698 (1)
$\alpha=\beta=\gamma$ (°)	90	
Unit cell volume (Å ³)	321.89 (2)	333.82 (1)
R _w (%)	3.7	11.7

Bond type	Bond length (Å)				
	NaCeW-a	NaCeW-b	Bond type	NaCeW-a	NaCeW-b
W1-O1	1.781	1.812	Ce1/Na1-O9	2.409	2.430
W1-O2					
W1-O3					
W1-O4					
W2-O5					
W2-O6					
W2-O7					
W2-O8					
W3-O10	1.801	1.791	Ce3/Na3-O1	2.458	2.433
W3-O15					
W3-O9					
W3-O16					
W4-O11					
W4-O12					
W4-O13					
W4-O14					

<i>Atom site label</i>	<i>Site</i>	<i>Fractional coordinates</i>			<i>Occupancy</i>	<i>U_{iso} (Å²)</i>
		<i>x</i>	<i>y</i>	<i>z</i>		
Ce1	2b	0.000	0.500	0.750	0.51 (2)	0.007 (1)
Ce2	2b	0.500	0.000	0.250	0.51 (2)	0.007 (1)
Na1	2b	0.000	0.500	0.750	0.48 (2)	0.007 (1)
Na2	2b	0.500	0.000	0.250	0.48 (2)	0.007 (1)
Ce3	2d	0.500	0.500	0.000	0.51 (2)	0.001 (2)
Ce4	2d	0.000	0.000	0.500	0.51 (2)	0.001 (2)
Na3	2d	0.500	0.500	0.000	0.48 (2)	0.001 (2)
Na4	2d	0.000	0.000	0.500	0.48 (2)	0.001 (2)
W1	2a	0.000	0.000	0.000	1 (1)	0.002 (1)
W2	2a	0.500	0.500	0.500	1 (1)	0.002 (1)
W3	2c	0.500	0.000	0.750	1 (1)	0.002 (1)
W4	2c	0.000	0.500	0.250	1 (1)	0.002 (1)
O1	8g	0.1598 (1)	0.2387 (1)	0.9199 (1)	1 (1)	0.009 (1)
O2	8g	0.8401 (1)	0.7614 (1)	0.9199 (1)	1 (1)	0.009 (1)
O3	8g	0.7612 (1)	0.1598 (1)	0.0800 (1)	1 (1)	0.019 (1)
O4	8g	0.2397 (1)	0.8401 (1)	0.0800 (1)	1 (1)	0.019 (1)
O5	8g	0.6598 (1)	0.7387 (1)	0.4199 (1)	1 (1)	0.009 (1)
O6	8g	0.3401 (1)	0.2612 (1)	0.4199 (1)	1 (1)	0.009 (1)
O7	8g	0.2612 (1)	0.6598 (1)	0.5800 (1)	1 (1)	0.019 (1)
O8	8g	0.7387 (1)	0.3401 (1)	0.5800 (1)	1 (1)	0.019 (1)
O9	8g	0.6583 (1)	0.2521 (1)	0.8251 (1)	1 (1)	0.014 (1)
O10	8g	0.3417 (1)	0.7578 (1)	0.8251 (1)	1 (1)	0.014 (1)
O11	8g	0.7529 (1)	0.6583 (1)	0.1748 (1)	1 (1)	0.040 (1)
O12	8g	0.2529 (1)	0.3417 (1)	0.1748 (1)	1 (1)	0.040 (1)
O13	8g	0.1581 (1)	0.7521 (1)	0.3251 (1)	1 (1)	0.014 (1)
O14	8g	0.8418 (1)	0.2478 (1)	0.3251 (1)	1 (1)	0.014 (1)
O15	8g	0.2478 (1)	0.1581 (1)	0.6748 (1)	1 (1)	0.040 (1)
O16	8g	0.7421 (1)	0.8418 (1)	0.6748 (1)	1 (1)	0.040 (1)

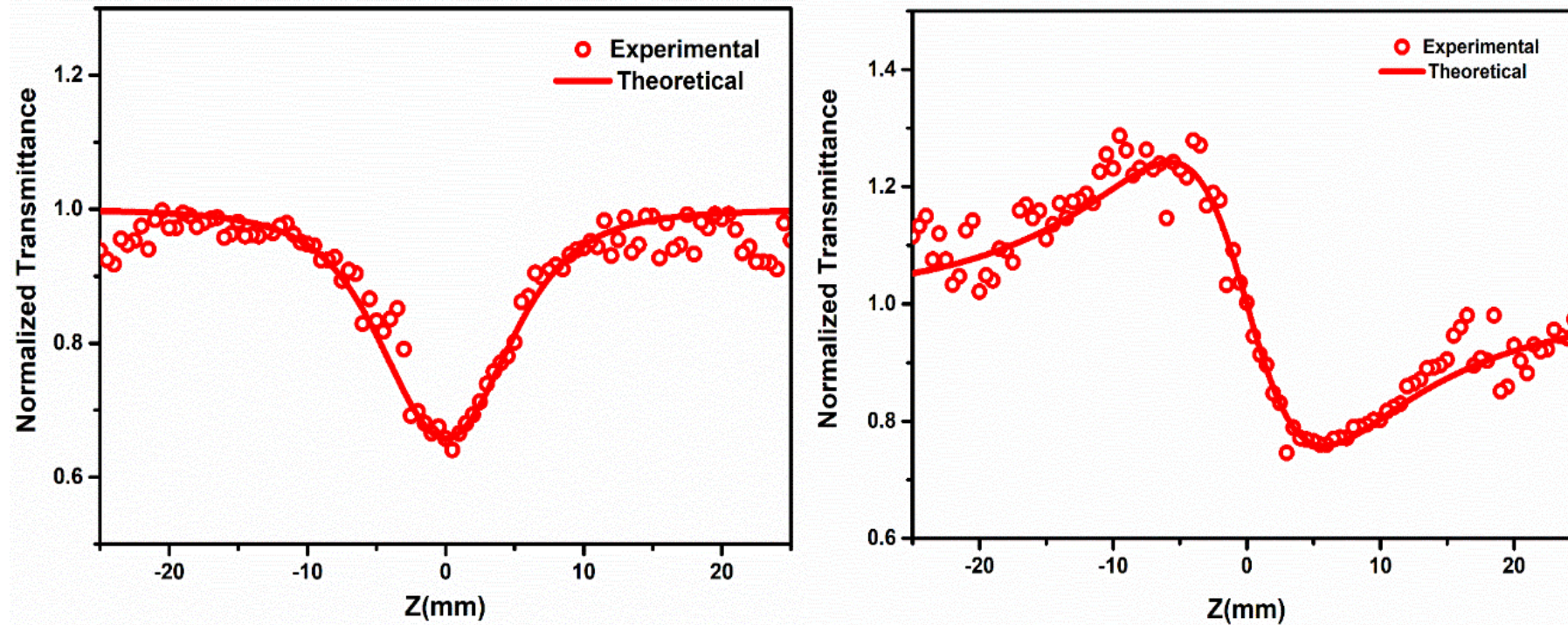
Atomic coordinates and thermal parameters obtained from the PDF refinements of NaCeW-a using $I\bar{4}$ model in $r=1.5$ to 3.5 Å.

Room temperature fluorescence studies



Optical excitation spectra at 529 nm emission and ii) optical emission spectra at 388 nm excitation of
a) NaCeW-a and b) NaCeW-b

Non linear third harmonic studies



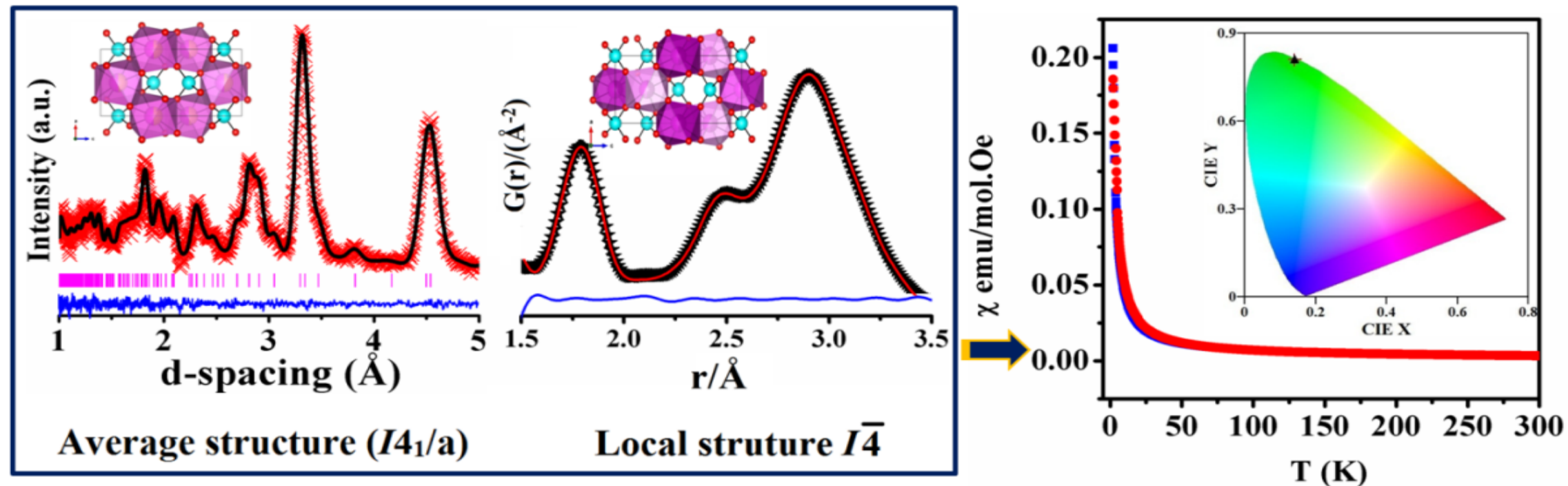
Open and closed aperture Z-scan trace of NaCeW-a

Sample	$B_{\text{eff}} \text{ (m}^2\text{/W)} \times 10^{-5}$	$n_2 \text{ (esu)} \times 10^{-5}$	$\text{Re } \chi^{(3)} \times 10^{-7} \text{ (esu)}$	$\text{Im } \chi^{(3)} \times 10^{-7} \text{ (esu)}$	$\chi^{(3)} \times 10^{-7} \text{ (esu)}$
NaCeW-a	9.76	5.75	6.66	2.03	6.96

Nonlinear optical parameters

Summary

Here we have described the solvothermal synthesis of nanocrystalline $\text{NaCe}(\text{WO}_4)_2$ materials with detailed elucidation of the average and local structure by Rietveld and Real-space refinement method.



Noncentrosymmetry in the local structure would be the one of the reason for the observed optical limiting and self defocusing THG properties. Furthermore, second harmonic properties are under investigation to probe the local structural variations. Thus, these new green emitting single phosphor could be potential material for solid state lighting and optoelectronic applications.

Acknowledgement

1. PhD supervisor Dr. Nalini G Sundaram for constant support and encouragement
2. Poornaprajna Institute of Scientific Research (PPISR) for research facilities.
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5. ADD2019 for this opportunity.
6. DST-SERB, INDIA for travel support.
7. Family and friends for their constant support.

Thank
You!

