Average and Local Structure of $NaCe(WO_4)_2$ Nanophosphor: Structure-Property Correlation

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Plan of the talk

1. Introduction

2. Synthesis and Experimental studies

3. Structural characterization of $NaCe(WO_4)_2$

    a) Average structure

    b) Local Structure

4. Discussion and Summary

Introduction

$[ARE(WO_4)_2]$

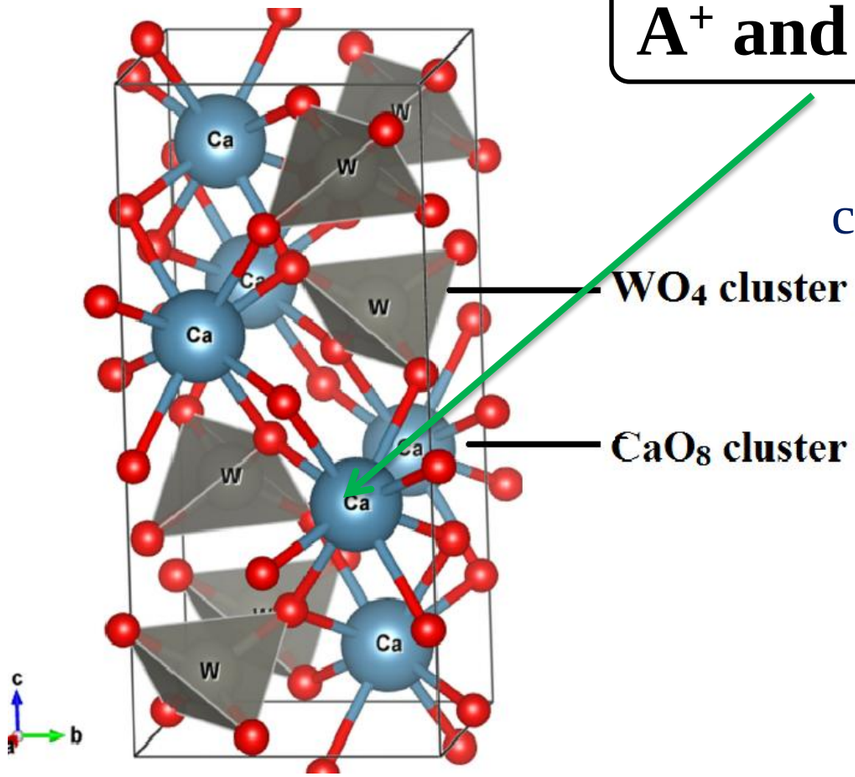
where A=Alkali metal ion and RE= TM (In/Y/Rareearths)

A^+ and RE^{3+}

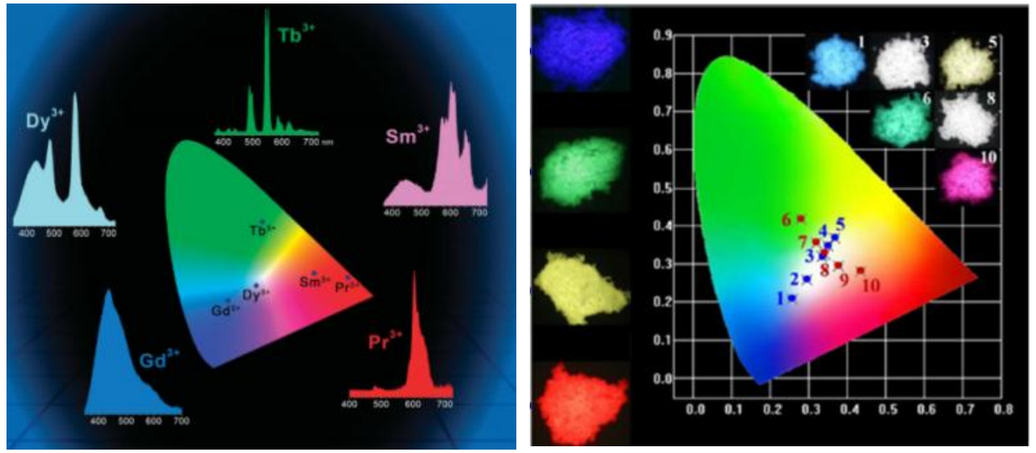
Shares same crystallographic site

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

Physiochemical properties

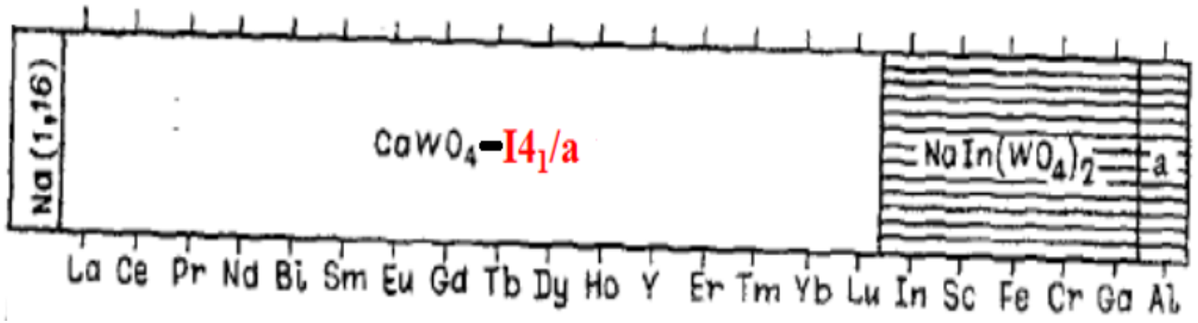


$CaWO_4$ Scheelite structure

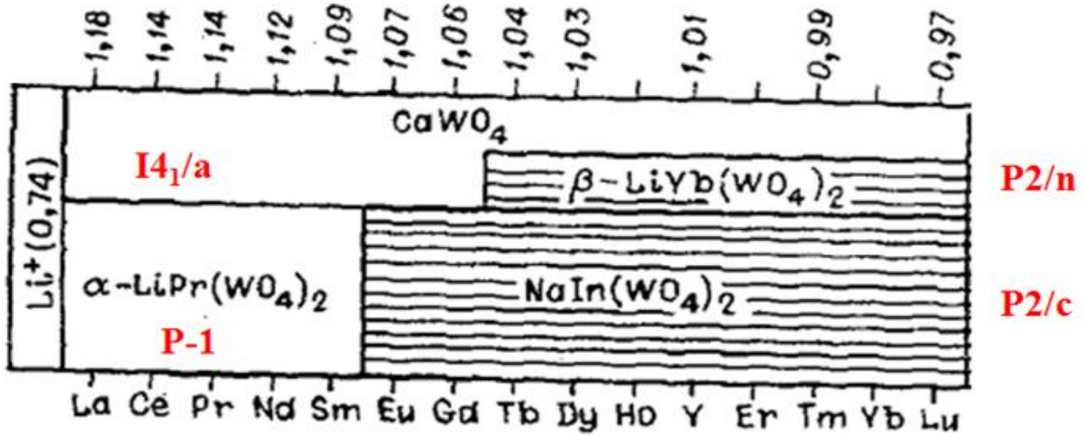


Optical properties

Motivation



$NaRE(WO_4)_2$



$LiRE(WO_4)_2$

Polymorphism

1. Triclinic, tetragonal, orthorhombic and monoclinic
2. Bulk materials
3. Solid state method at high temperature

P.V. Klevtsov et.al Academy of Sciences of the USSR, 12, 1977
E. Pawel Tomaszewski A Multinational Journal, 38, 2012

Synthesis-Solvothermal method

Stochiometric amount of all precursors

Dissolved in MilliQ water

Precursor solution was mixed slowly

Transferred to Teflon lined stainless steel autoclave

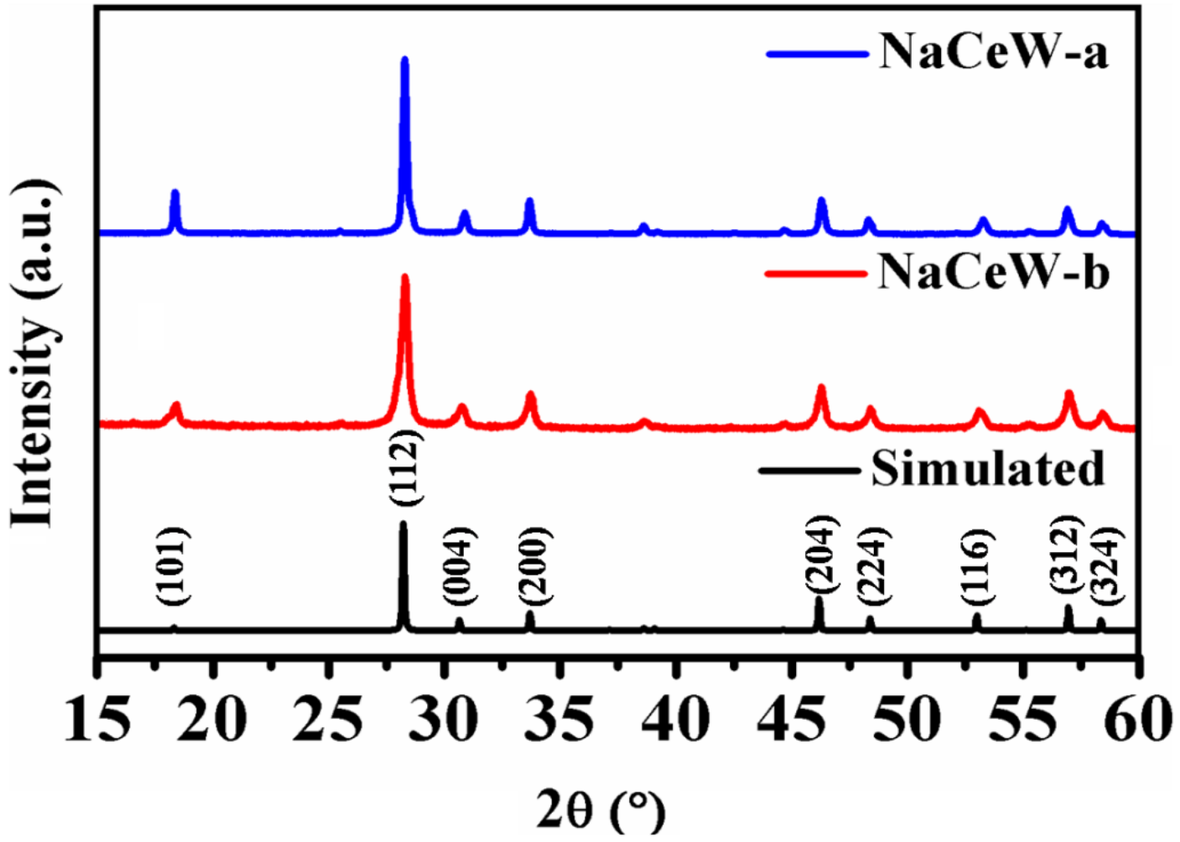
200 °C and 30hr

Final product

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

Structural Characterization of $NaCe(WO_4)_2$

Effect of solvent on phase formation and crystallinity

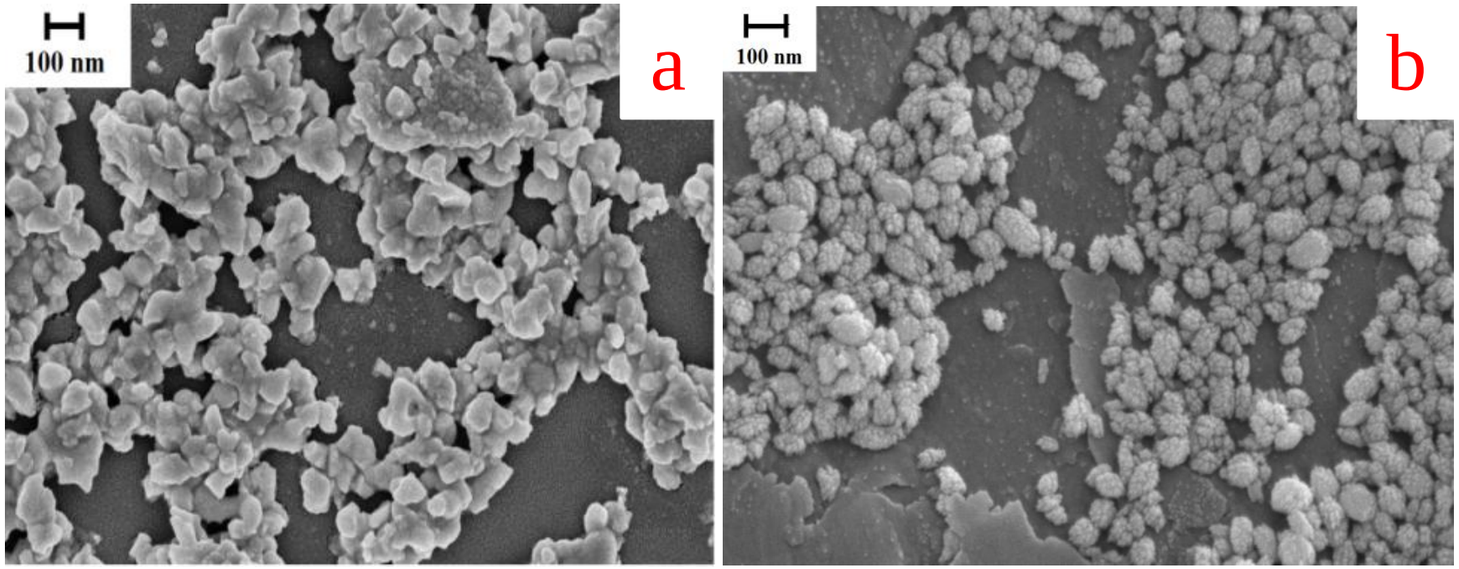


Powder XRD patterns

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

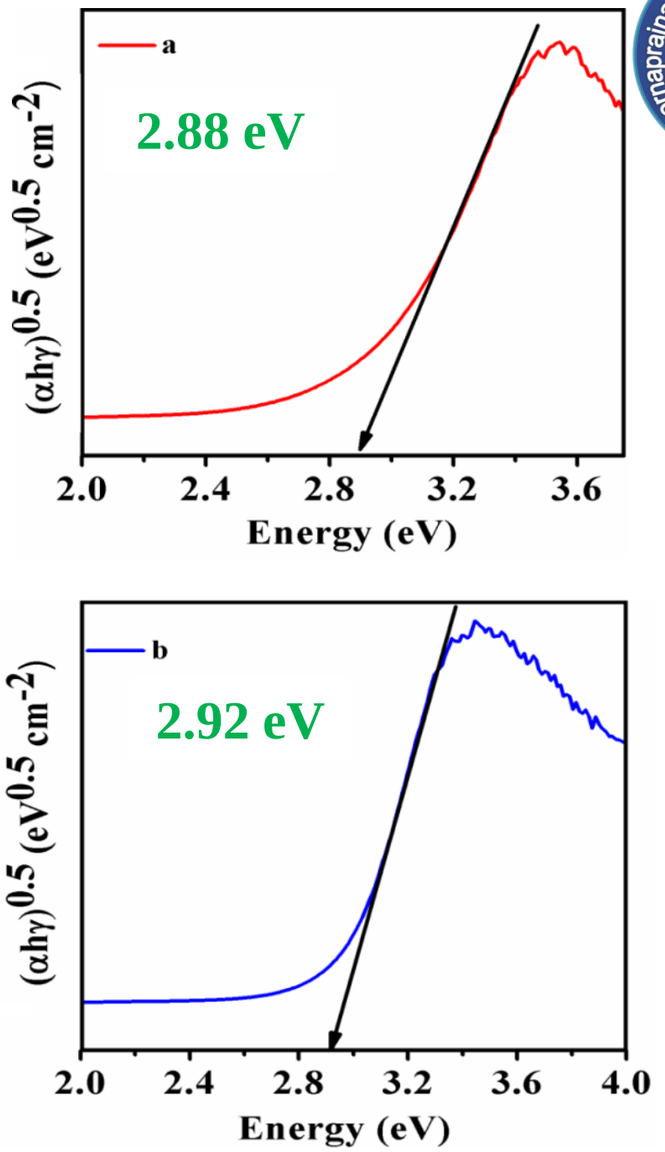
Microscopy and UV-Diffuse Reflectance Studies



FESEM images of as prepared $NaCe(WO_4)_2$ nanoparticles
a) NaCeW-a and b) NaCeW-b

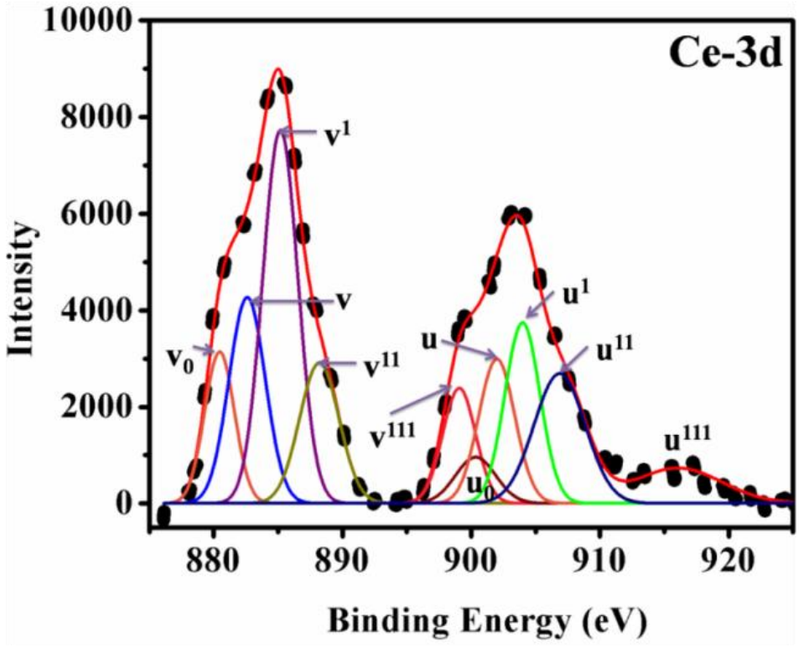
a) Irregular sized agglomerated particles of smooth morphology and particle size in the range 150-200 nm

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



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

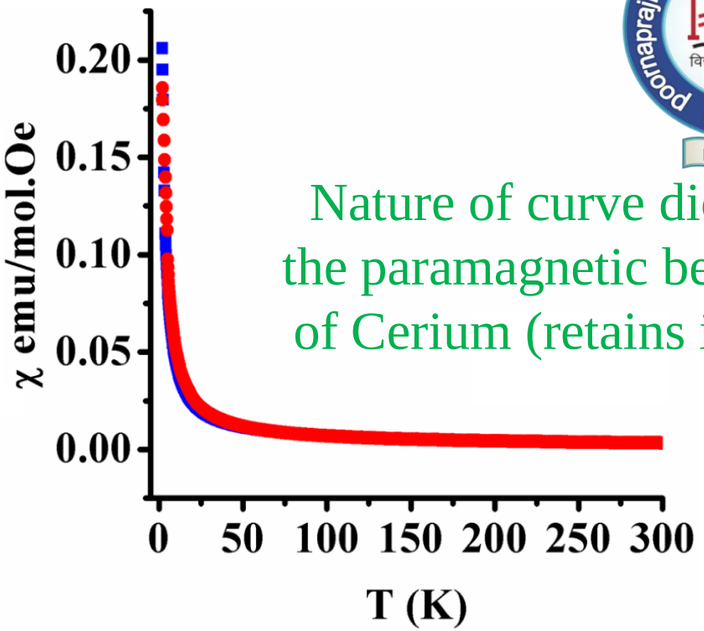
X-ray Photon Spectroscopy and Magnetic studies



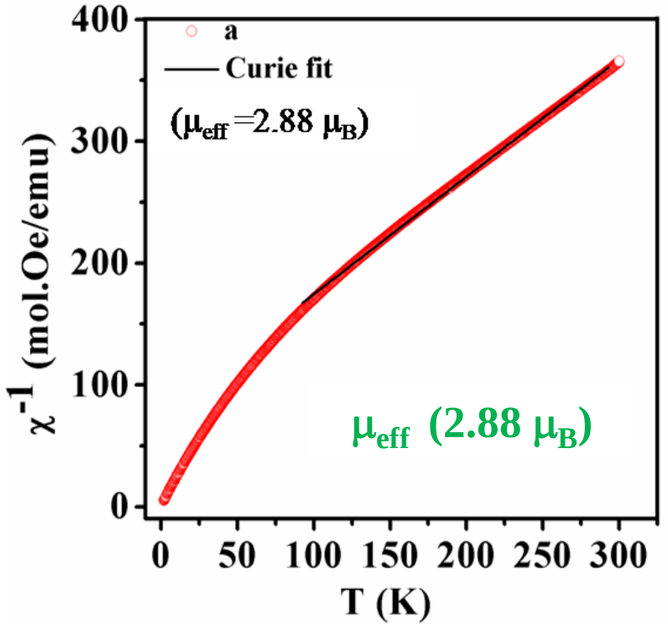
High resolution XPS spectrum of Ce-3d with the corresponding deconvoluted peaks.

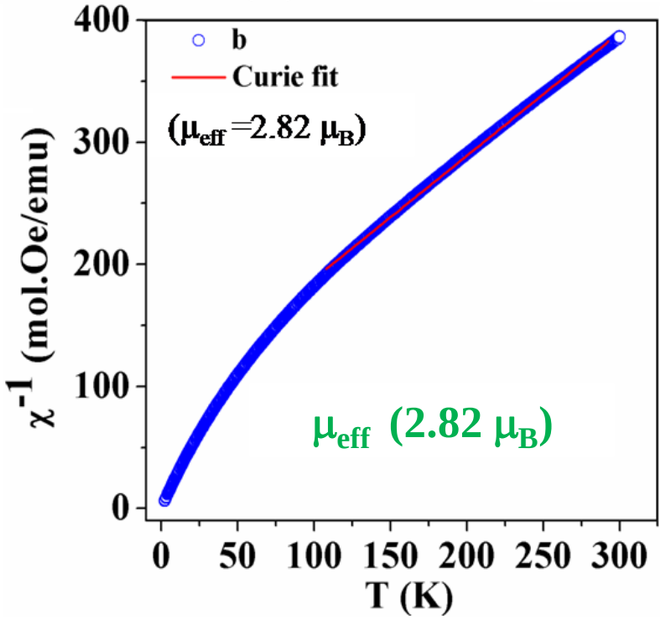
Confirms the presence of +3 valence state of cerium ion

Temperature dependent magnetic susceptibility (χ) against temperature



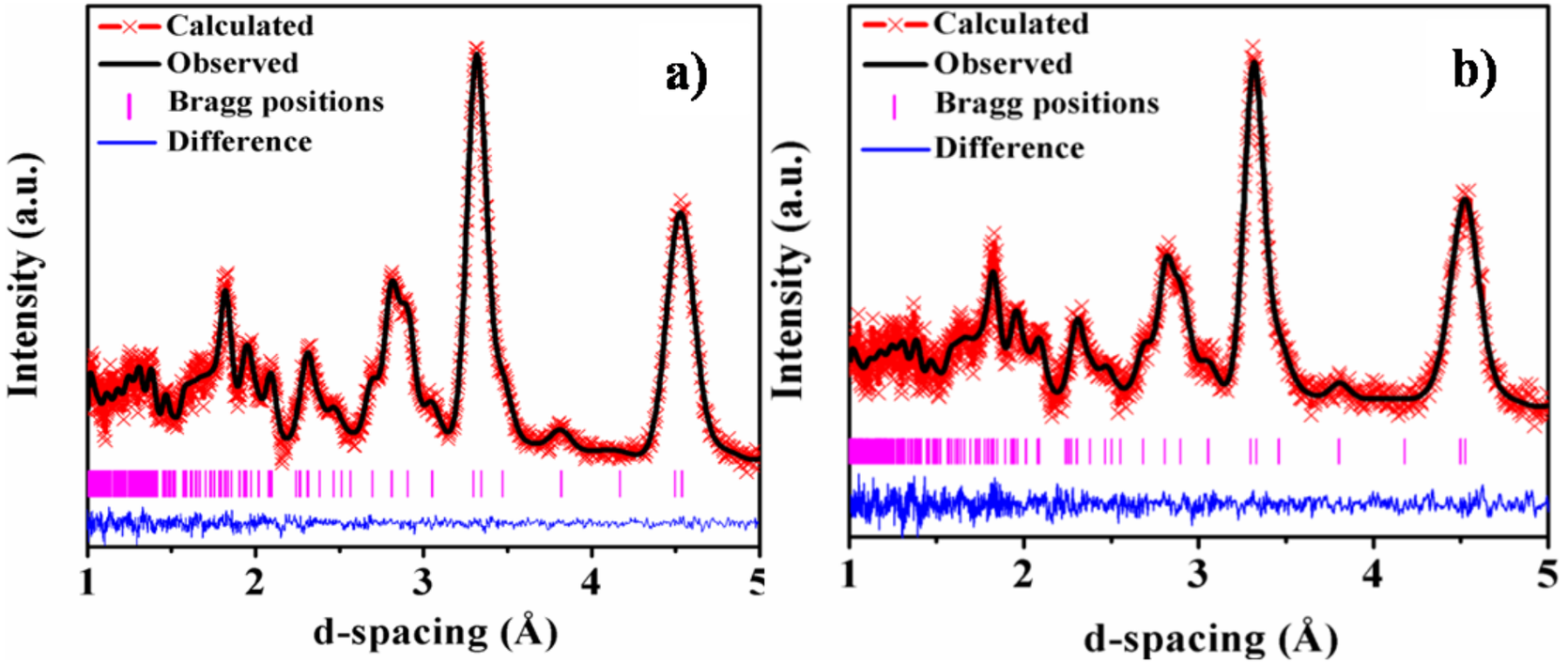
Nature of curve dictates the paramagnetic behavior of Cerium (retains its +3)





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 $NaCe(WO_4)_2$ synthesized by solvothermal method
a) NaCeW-a and b) NaCeW-b

$Na_{0.5}Ce_{0.5}MoO_4$ as standard model (ICSD No 67493) crystallizing in $I4_1/a$

Crystallographic data of $NaCe(WO_4)_2$ obtained from Rietveld refinements using NPD data, a) NaCeW-a and b) NaCeW-b

Crystallographic data	NaCeW-a	NaCeW-b
a=b (Å)	5.332 (2)	5.334 (2)
c (Å)	11.677 (2)	11.681 (2)
α=β=γ (°)	90	90
Unit cell volume (Å^3)	332.06 (2)	332.37 (2)

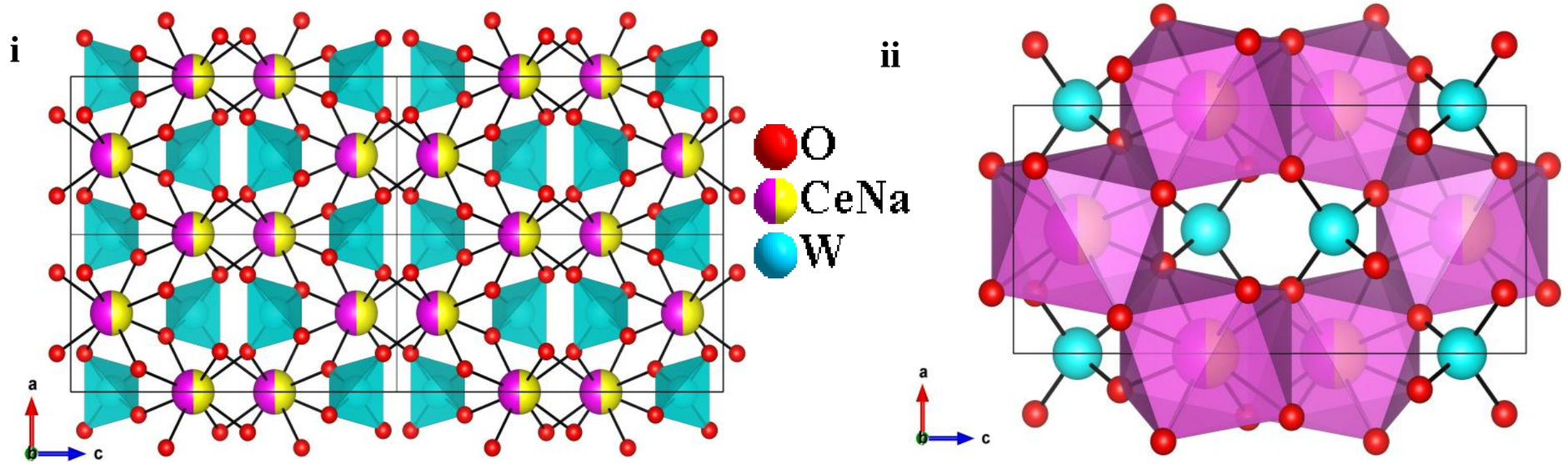
Material	NaCeW-a	NaCeW-b
RWp (%)	5.0	4.4
Rp (%)	4.1	3.4
$RI_{(cal)}$ (%)	6.5	6.7

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

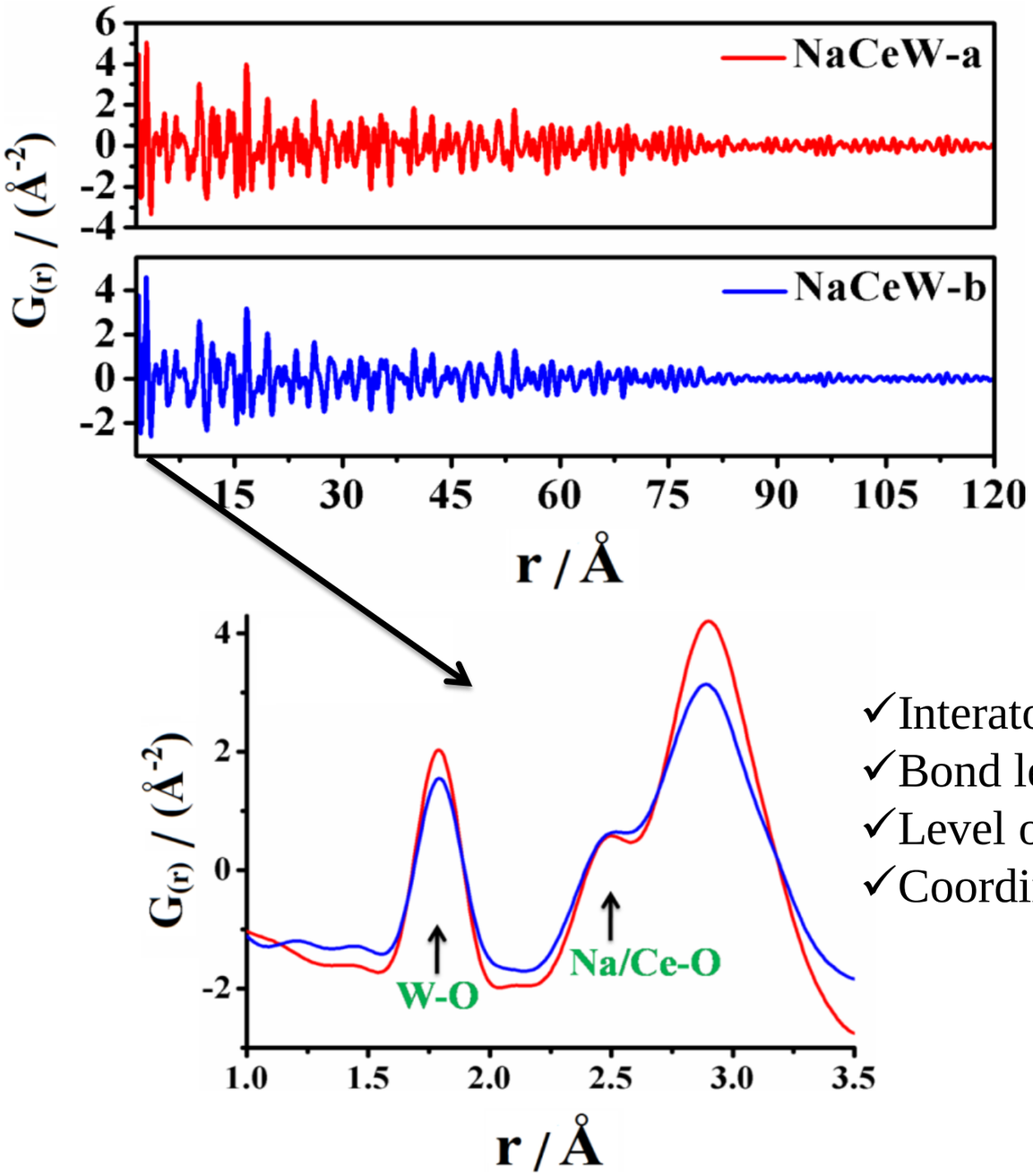
Bond type	***CN***	***Bond length (Å)***	
		NaCeW-a	***NaCeW-b***
Na/Ce-O	4	2.520 (2)	2.518 (2)
Ce/Na-O	4	2.567 (3)	2.535 (3)
W-O	4	1.740 (2)	1.787 (2)

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

Real-space Rietveld

NOMAD, ORNL, US

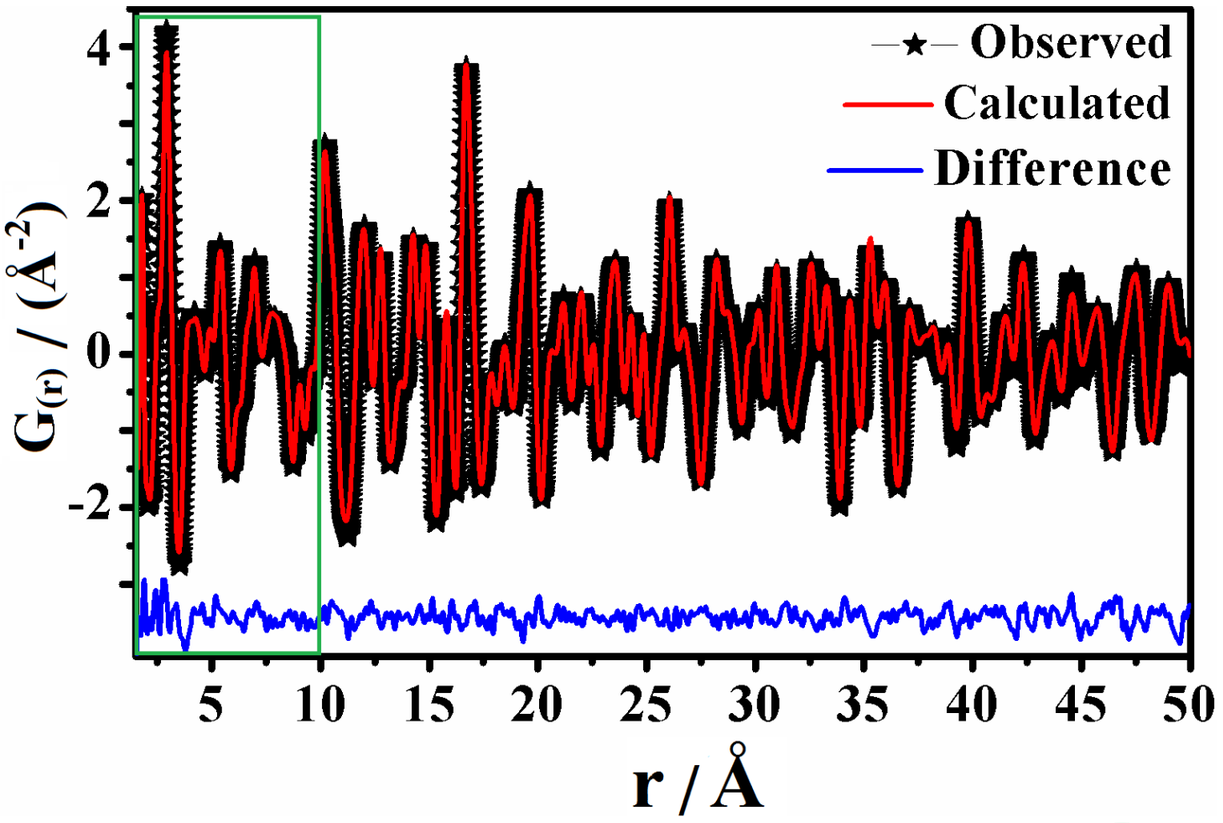
Q_{max} = 31.41 Å^{-1}
295 K
r=1.5 to 50 Å
Qdamp=0.01765
Qbroad=0.01918

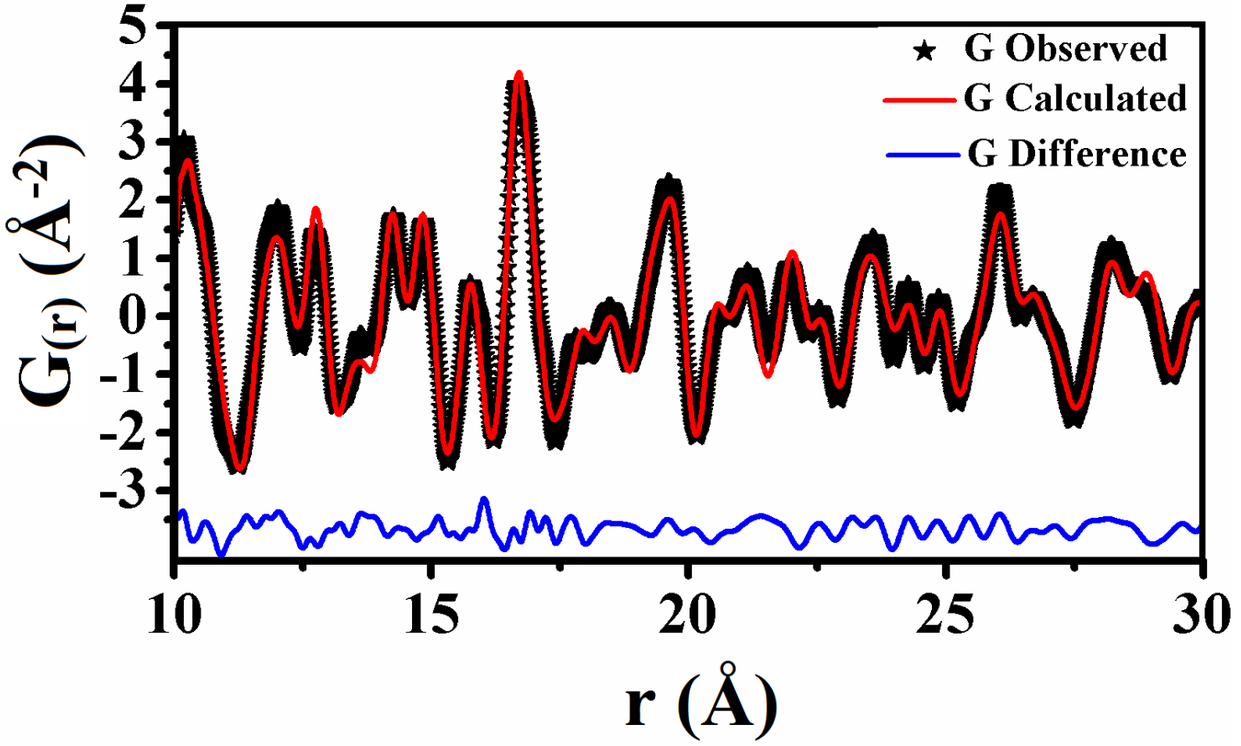


- ✓Interatomic distances
- ✓Bond lengths
- ✓Level of disorder
- ✓Coordination number

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

Centrosymmetric $I4_1/a$ model from Rietveld refinement

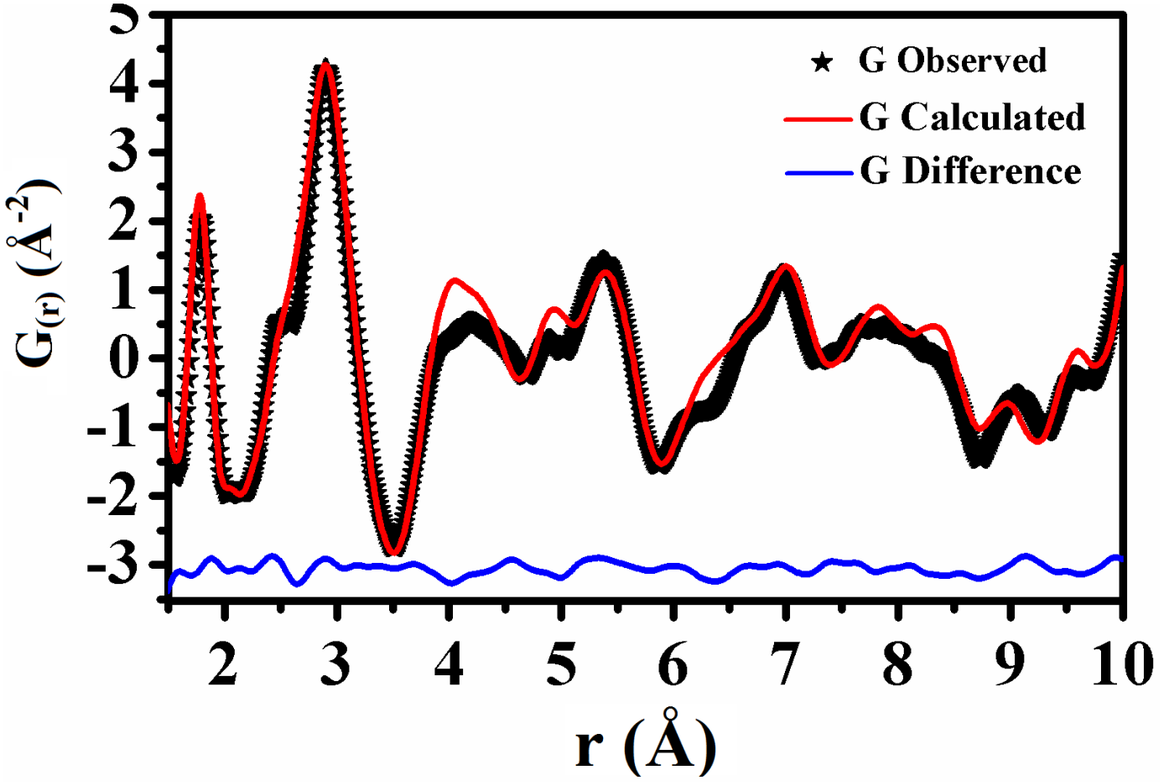




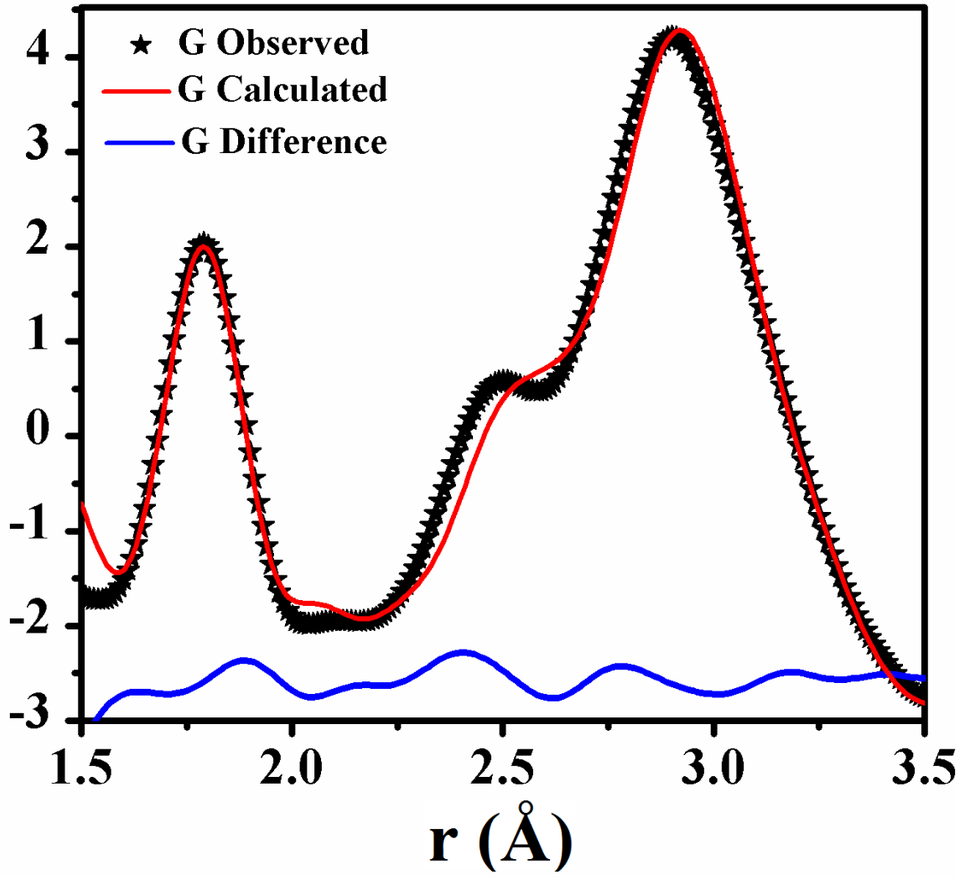
Long r-range

Observed (black), calculated (red) and difference PDF plot (blue) of NaCeW-a with R_{wp}= 9.9 %. Green box indicates the region with relatively poor fit below 10 Å.

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

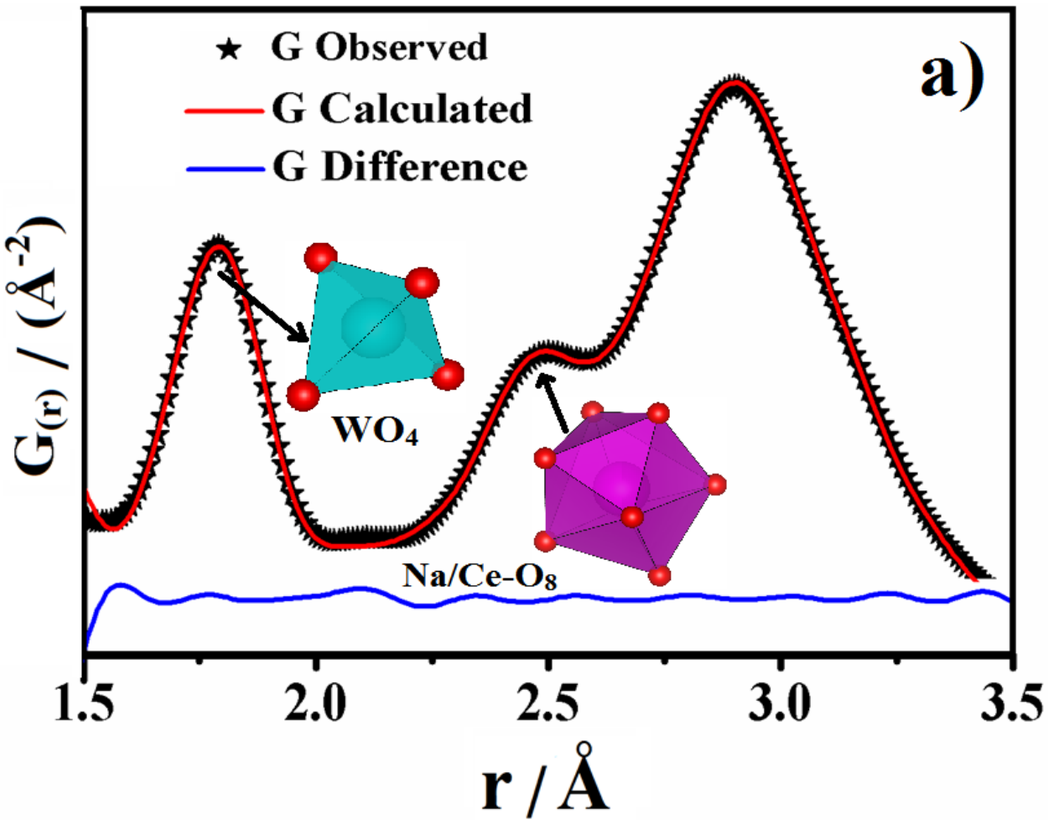


Medium r-range

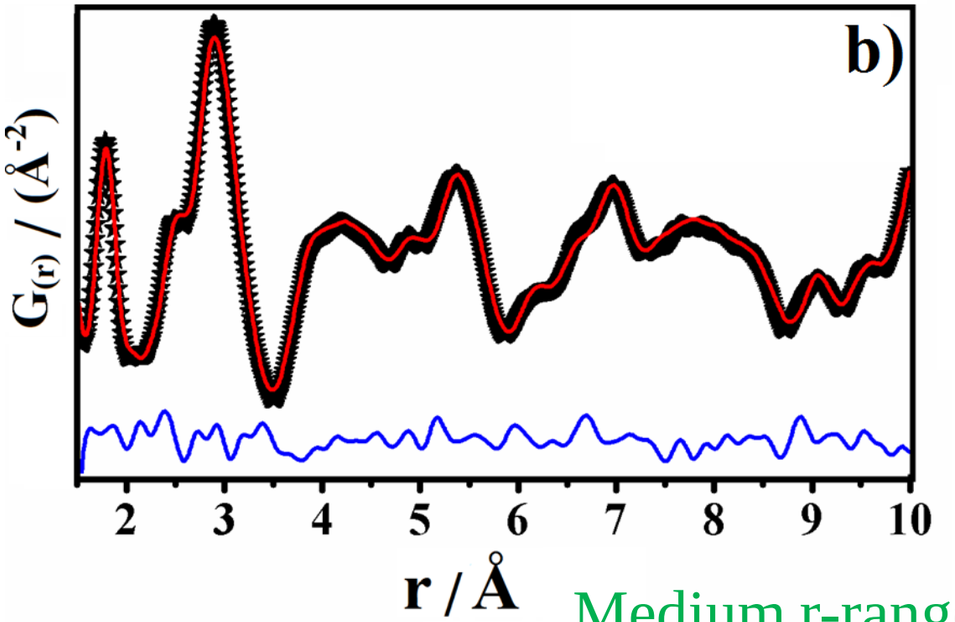


Short r-range

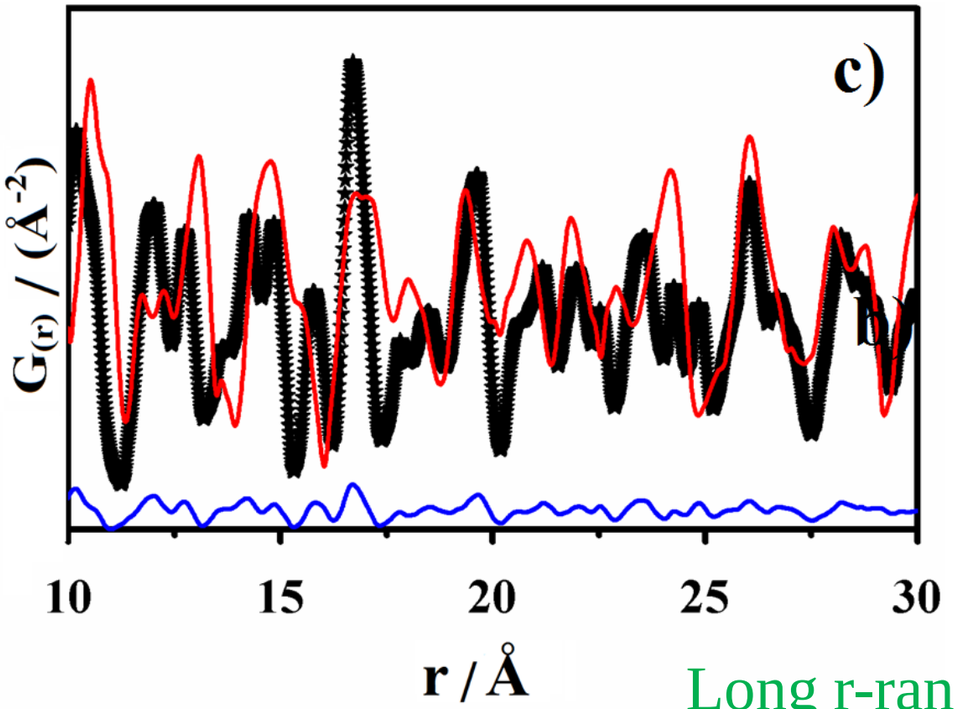
Noncentrosymmetric ($I\bar{4}$ model)
[$LiYb(MoO_4)_2$ (ICSD No: 152282)]



Short r-range

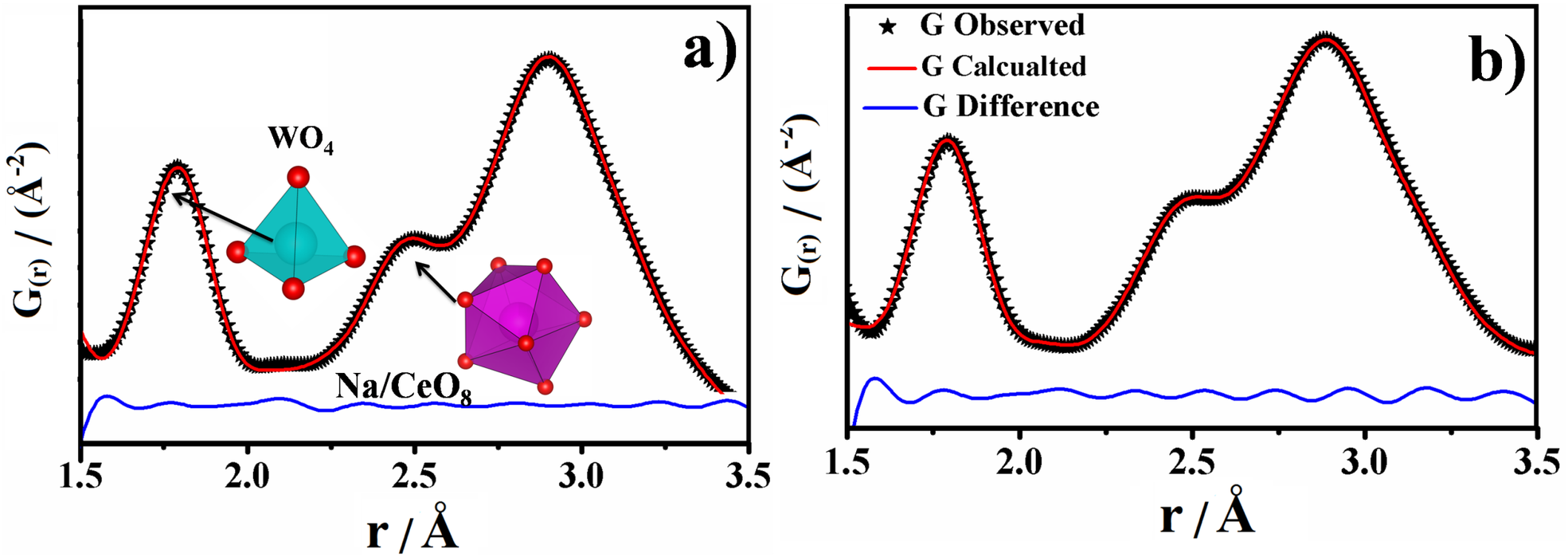


Medium r-range



Long r-range

Noncentrosymmetric $I\bar{4}$ model

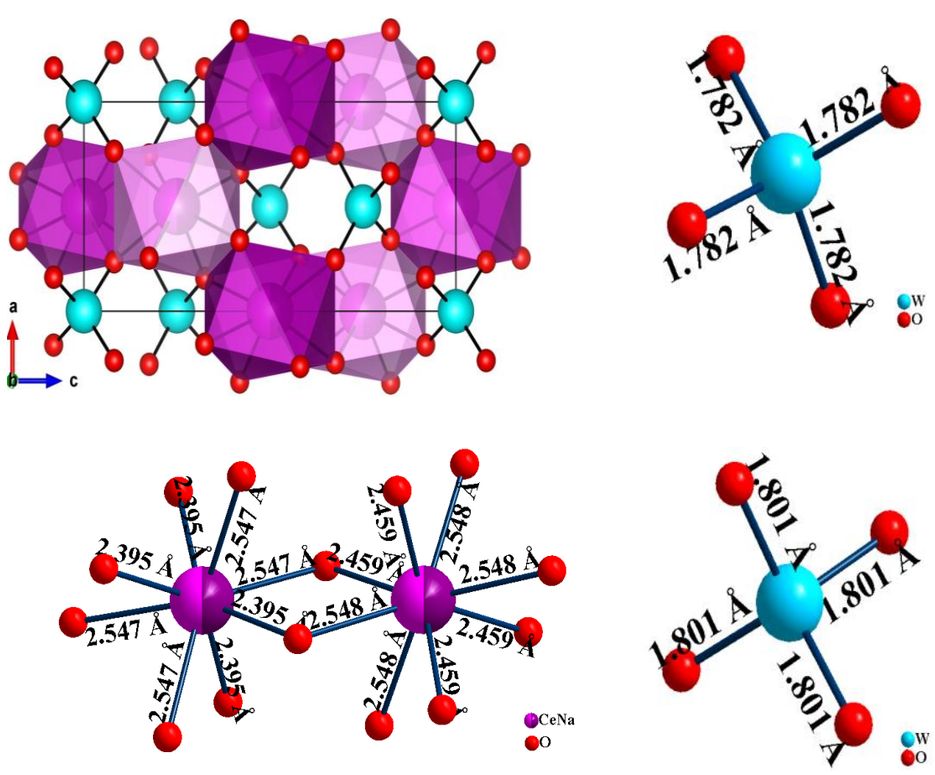


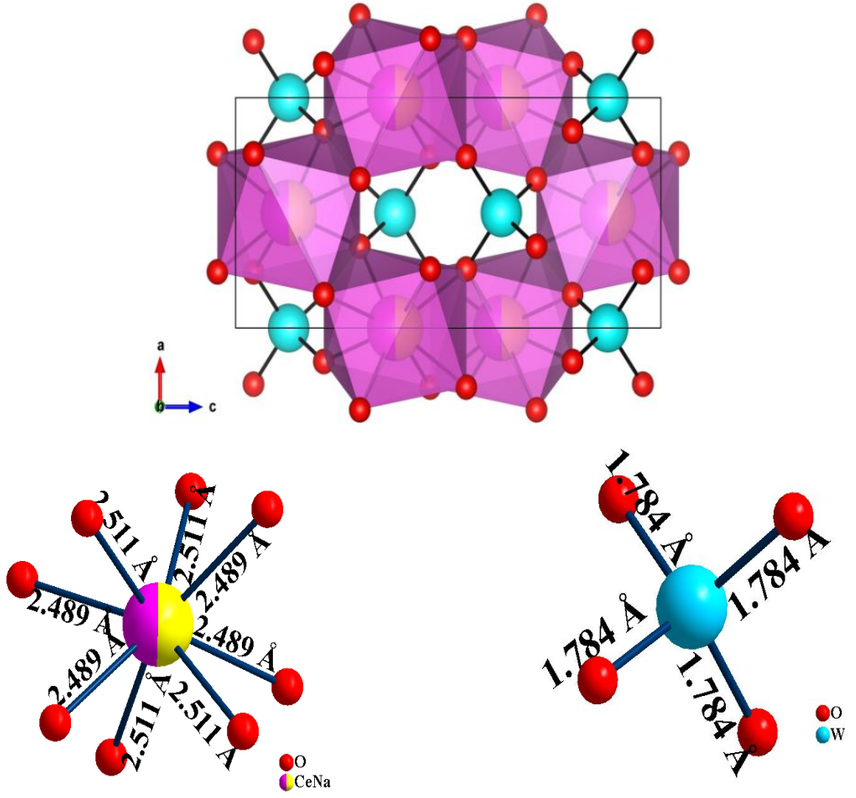
Observed (black), calculated (red) and difference PDF plot (blue)
of NaCeW-a and NaCeW-b

Structural variations in average and local structure of $NaCe(WO_4)_2$

Local structure *I*-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.

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)
α=β=γ (°)	90	
Unit cell volume (Å^3)	321.89 (2)	333.82 (1)
R_W (%)	3.7	11.7

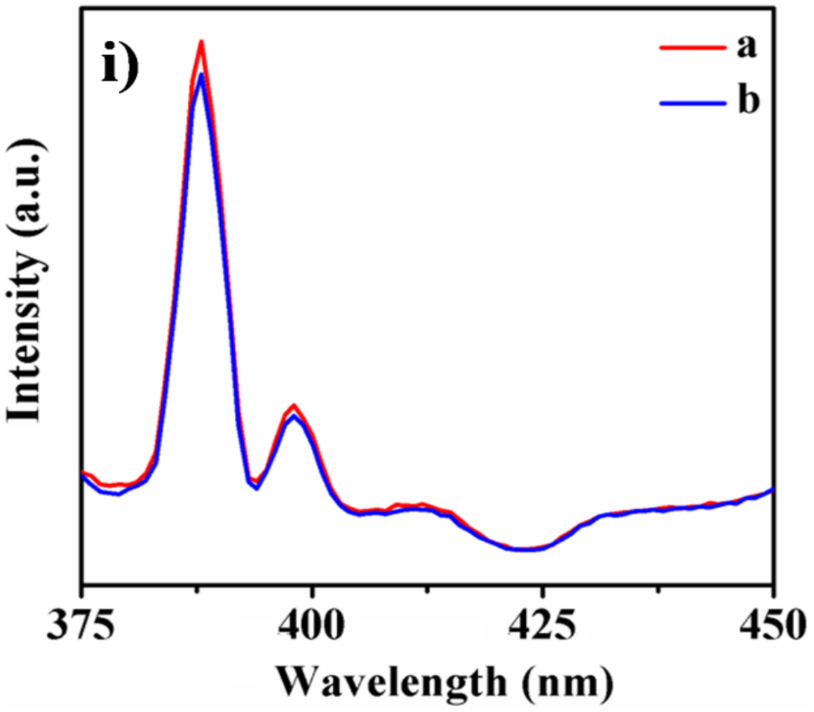
Selected bond distances in NaCeW-a and NaCeW-b via PDF refinements from r=1.5 to 3.5 Å using $I\bar{4}$ model.

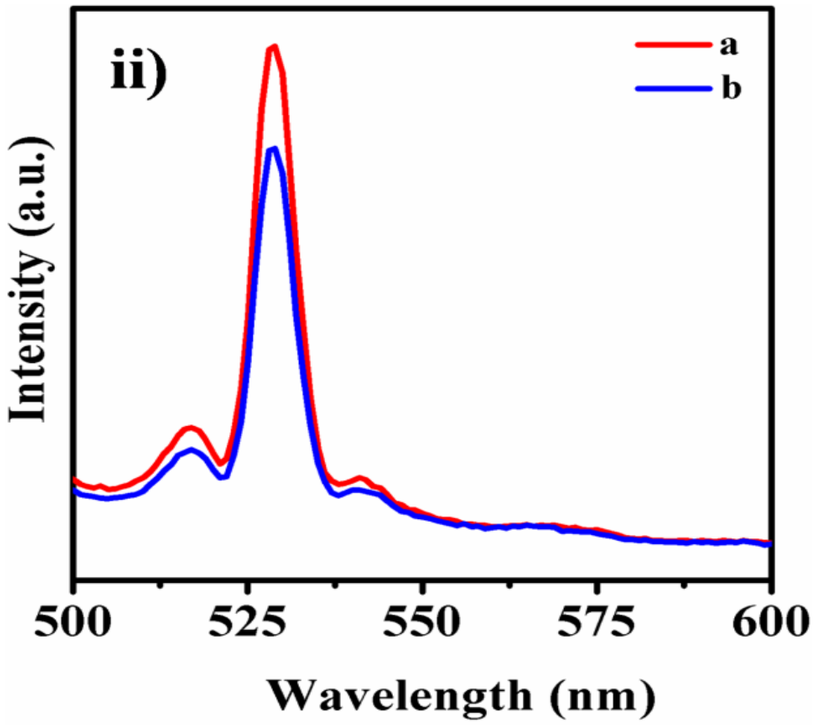
Bond type	***Bond length (Å)***				
	NaCeW-a	***NaCeW-b***	***Bond type***	***NaCeW-a***	***NaCeW-b***
W1-O1	1.781	1.812	Ce1/Na1-O9	2.409	2.430
W1-O2			Ce1/Na1-O10		
W1-O3			Ce1/Na1-O15		
W1-O4			Ce1/Na1-O16		
W2-O5			Ce2/Na2-O11		
W2-O6			Ce2/Na2-O12		
W2-O7			Ce2/Na2-O13		
W2-O8			Ce2/Na2-O14		
W3-O10	1.801	1.791	Ce3/Na3-O1	2.458	2.433
W3-O15			Ce3/Na3-O2		
W3-O9			Ce3/Na3-O3		
W3-O16			Ce3/Na3-O4		
W4-O11			Ce4/Na4-O5		
W4-O12			Ce4/Na4-O6		
W4-O13			Ce4/Na4-O7		
W4-O14			Ce4/Na4-O8		

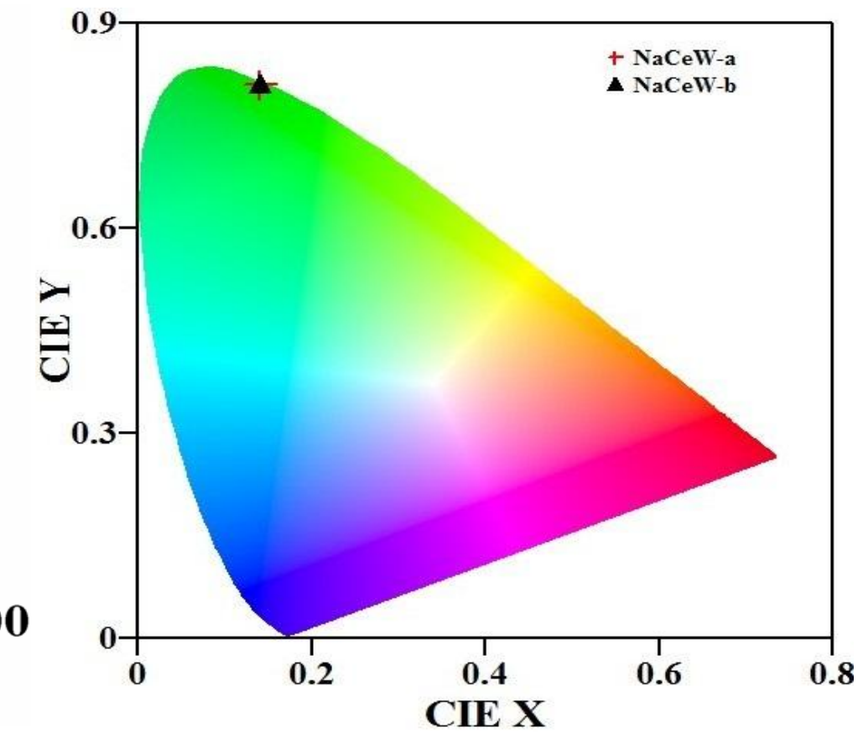
Atom site label	Site	Fractional coordinates			Occupancy	U_{iso} (Å^2)
		x	*y*	*z*		
Ce1	2b	0.000	0.500	0.750	0.51 (2)	0.007 (1)
Ce2	2b	0.500	0.000	0.250	0.51 (2)	0.007 (1)
Na1	2b	0.000	0.500	0.750	0.48 (2)	0.007 (1)
Na2	2b	0.500	0.000	0.250	0.48 (2)	0.007 (1)
Ce3	2d	0.500	0.500	0.000	0.51 (2)	0.001 (2)
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.

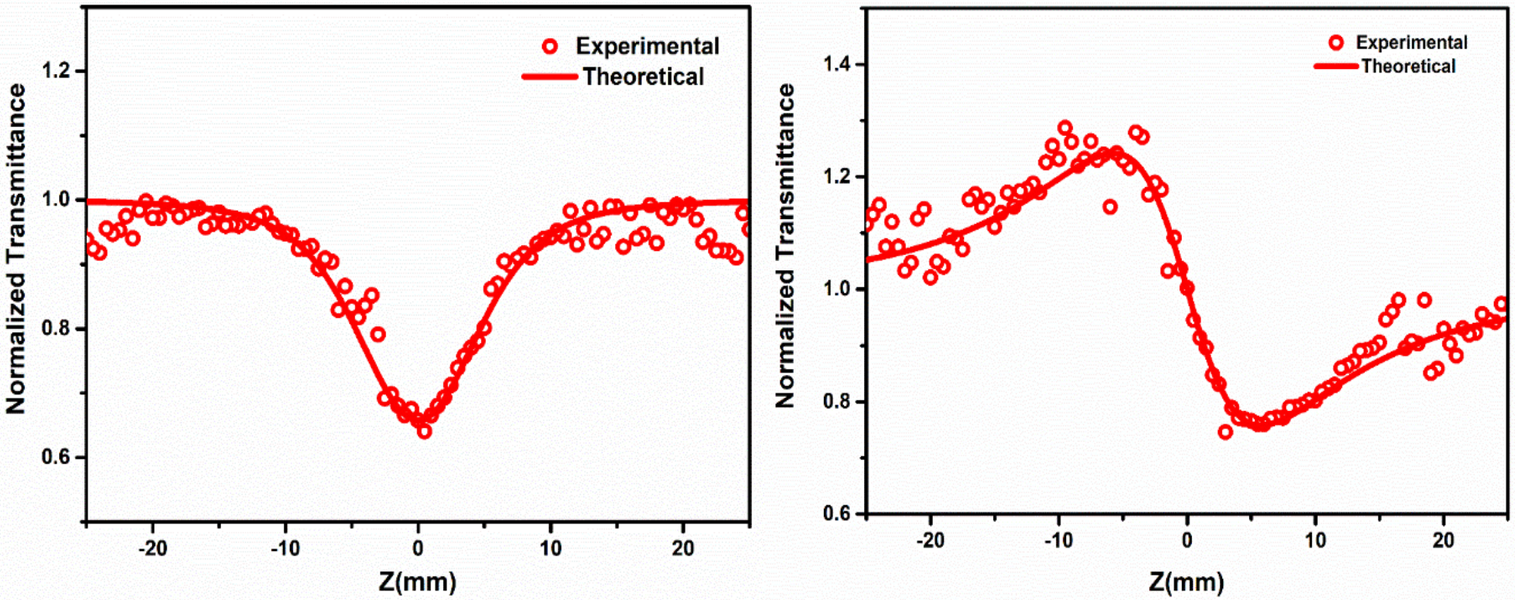






Optical excitation spectra at 529 nm emission and ii) optical emission spectra at 388 nm excitation of a) NaCeW-a and b) NaCeW-b

Non linear third harmonic studies



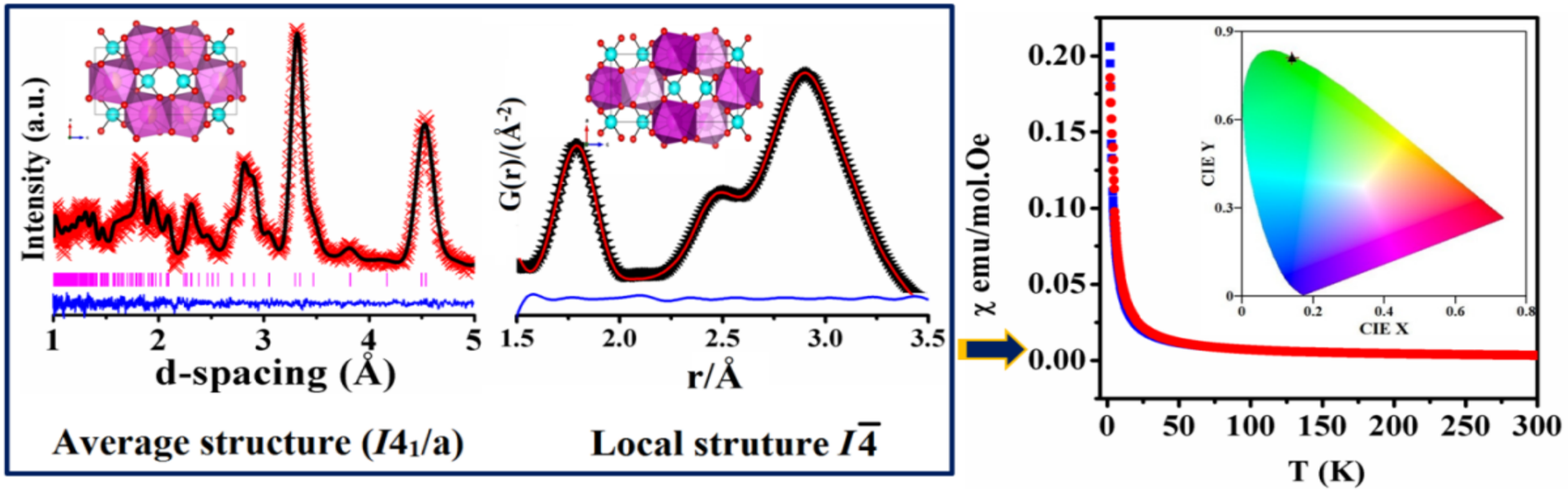
Open and closed aperture Z-scan trace of NaCeW-a

Sample	B_{eff} $(m^2/W)\times10^{-5}$	n_2 (esu) $\times10^{-5}$	Re $\chi^{(3)}\times10^{-7}$ (esu)	Im $\chi^{(3)}\times10^{-7}$ (esu)	$\chi^{(3)}\times10^{-7}$(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 $NaCe(WO_4)_2$ materials with detailed elucidation of the average and local structure by Rietveld and Real-space refinement method.



Additionally the noncentrosymmtery 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. Therefore, these new green emitting single phosphor could be potential material for solid state lighting and optoelectronic applications.

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2. Poornaprajna Institute of Scientific Research (PPISR) for research facilities.
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6. DST-SERB, INDIA for travel support.
7. Family and friends for their constant support.


Thank
You!