

Oxygen Vacancy Mediated Local Symmetry Breaking driven Intense

Raman Modes In BaZrO₃



Presented by

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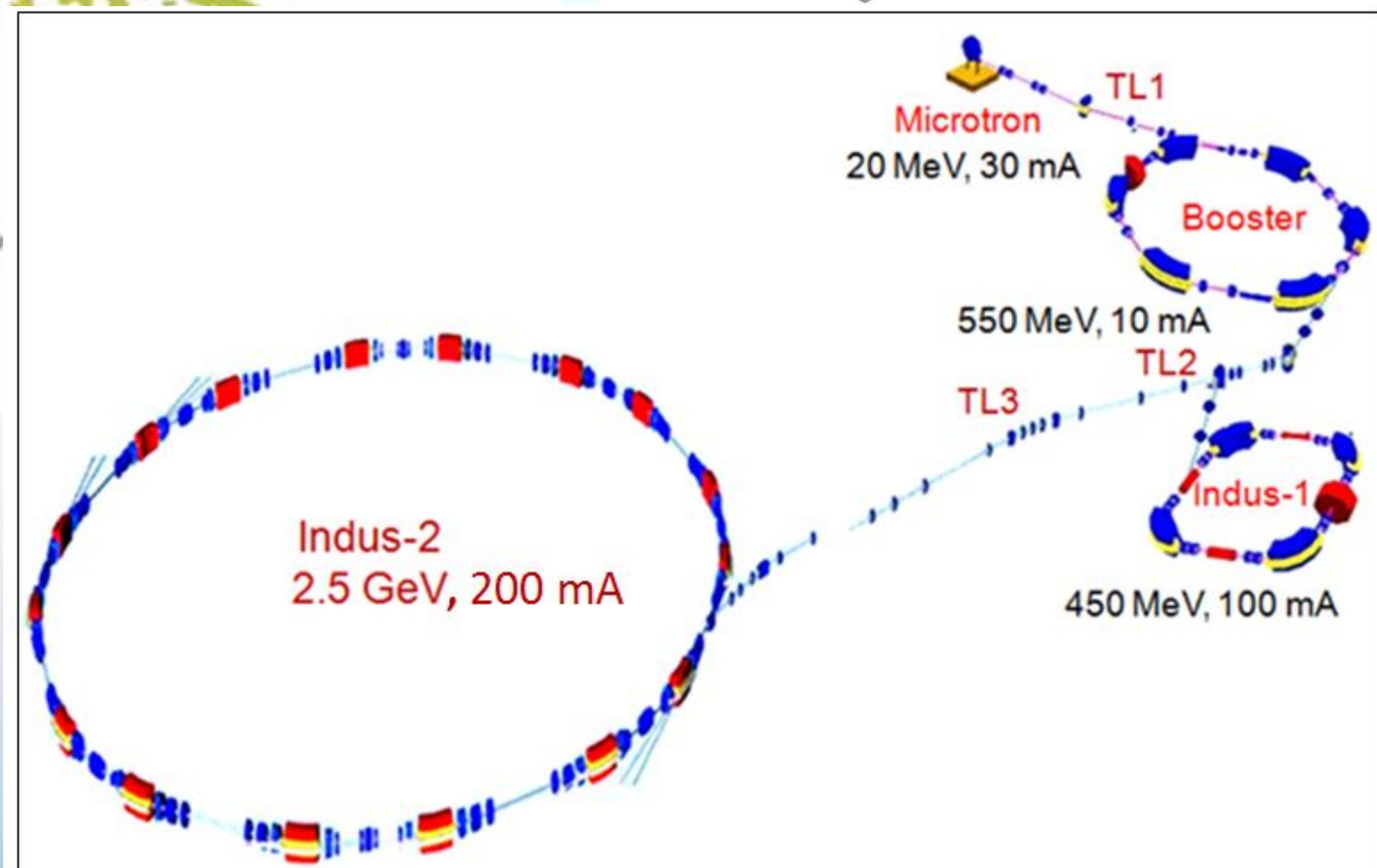
Scientist-F



Co-Supervisor:

Dr. Debalaya Sarker

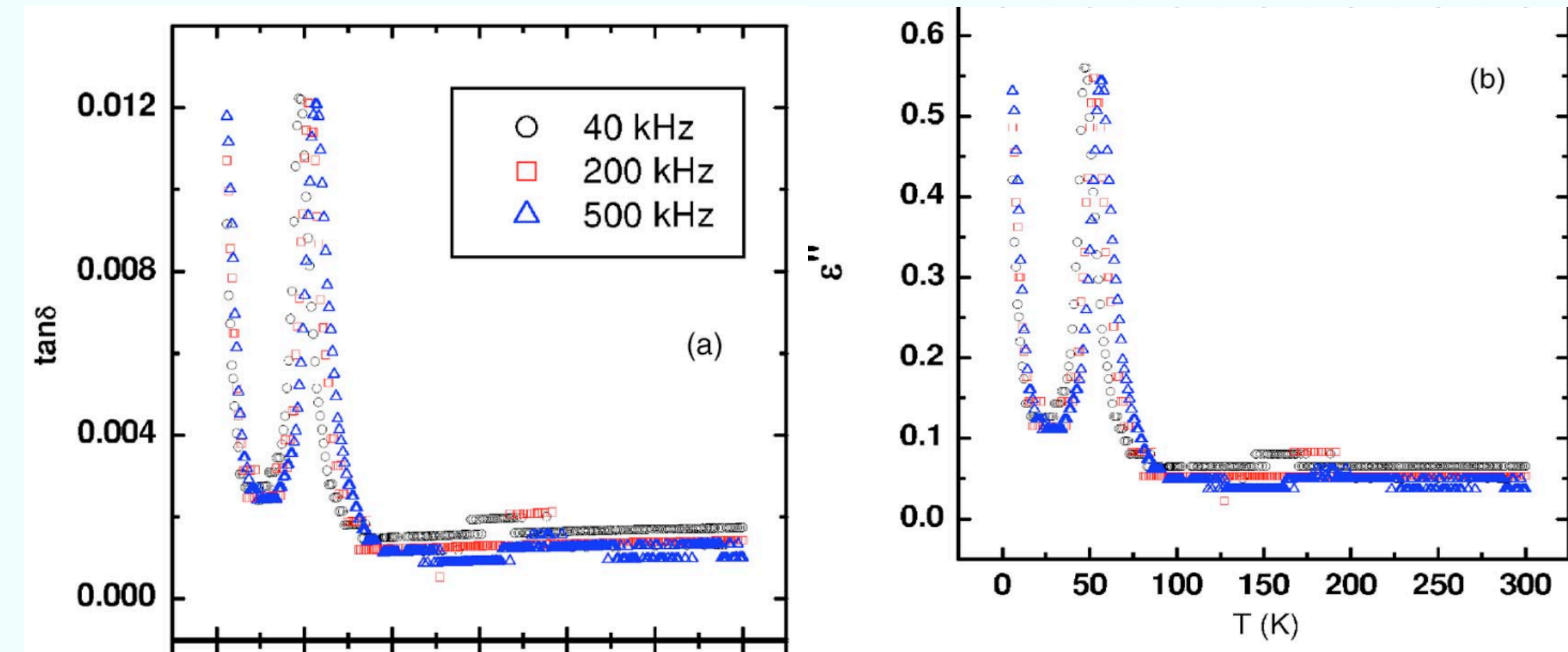
Scientist-D



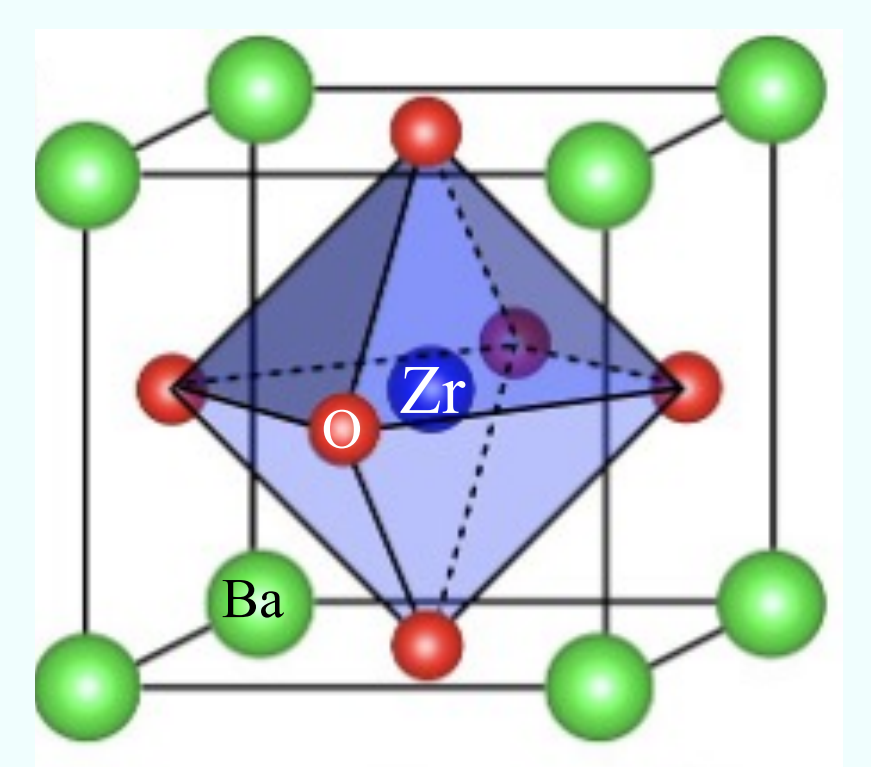
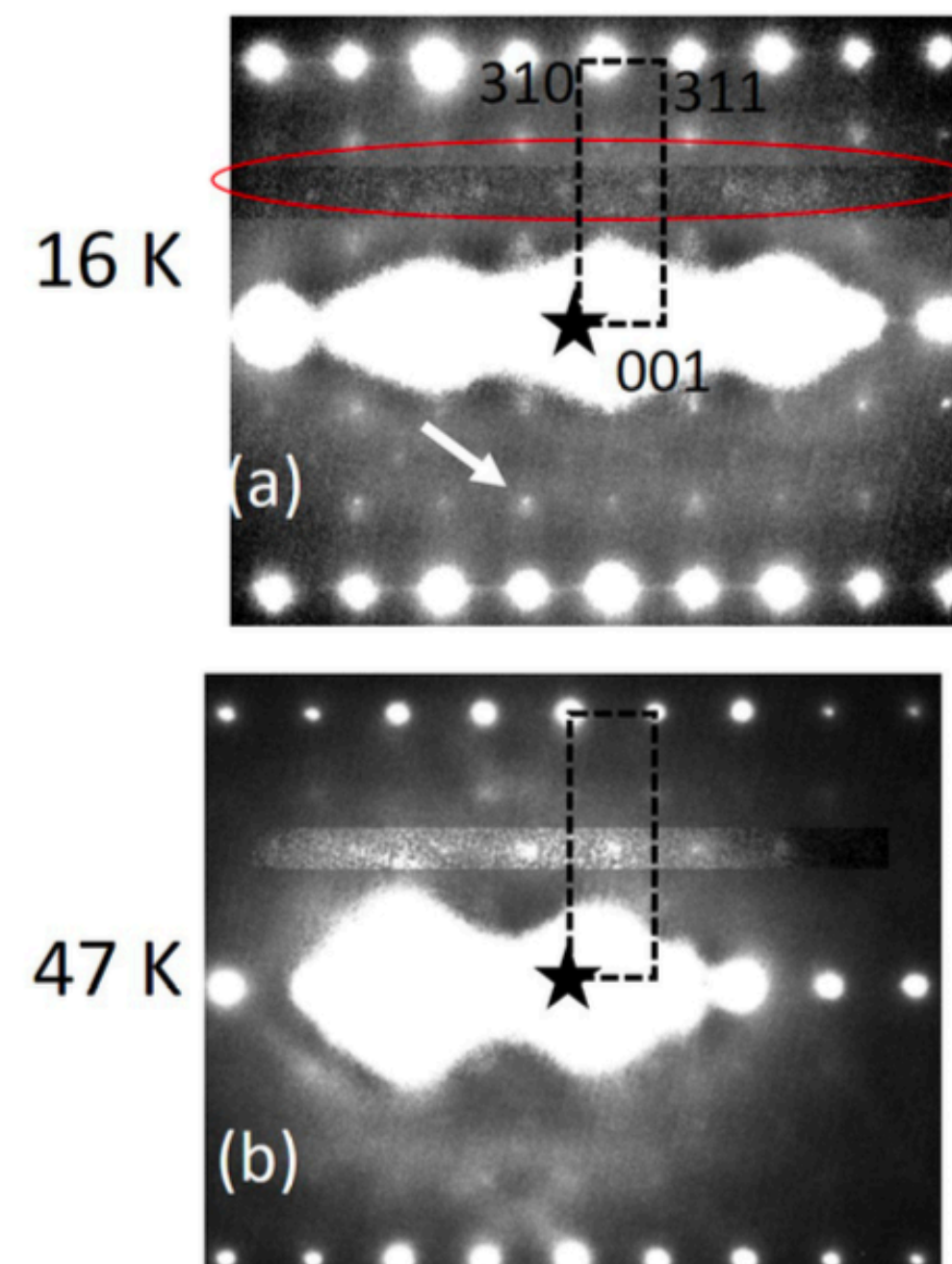
Outlines:

1. Introduction
2. Synthesis Mechanism
3. Results & Discussions
 - a. Structural Characterisation (XRD)
 - b. X-Ray Photoelectron Spectroscopy (XPS)
 - c. UV-Vis. & FTIR Spectroscopy
 - d. Extended X-Ray Absorption Fine Structure (EXAFS)
 - e. Raman Spectroscopy
4. Overall Conclusions & Future Scope
5. Acknowledgments

1. Introduction



A.R. Akbarzadeh, et.al, *Phys. Rev. B* **72**,205104 (2005)

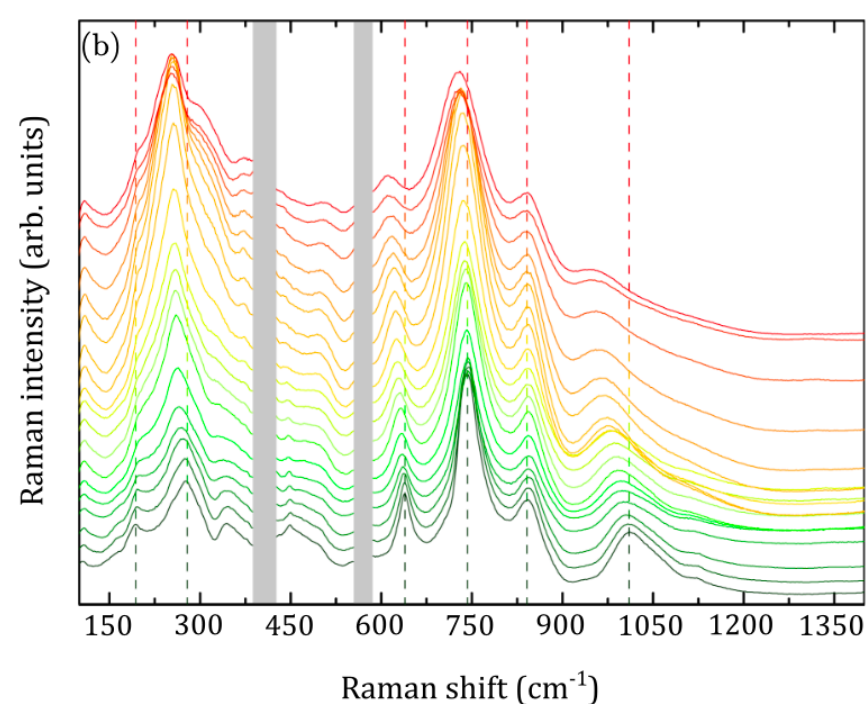
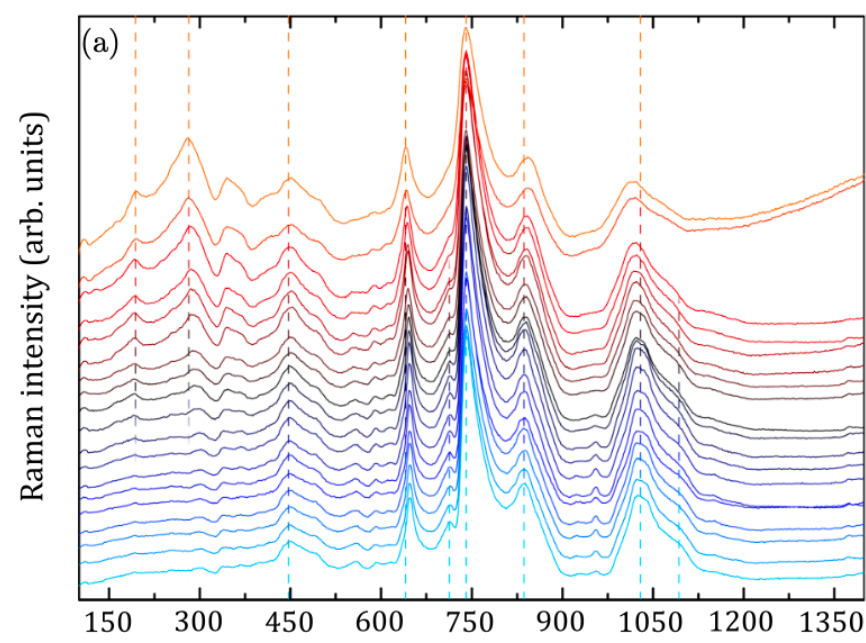


BaZrO₃ Centro-symmetric cubic system

Net change in Polarizability = 0

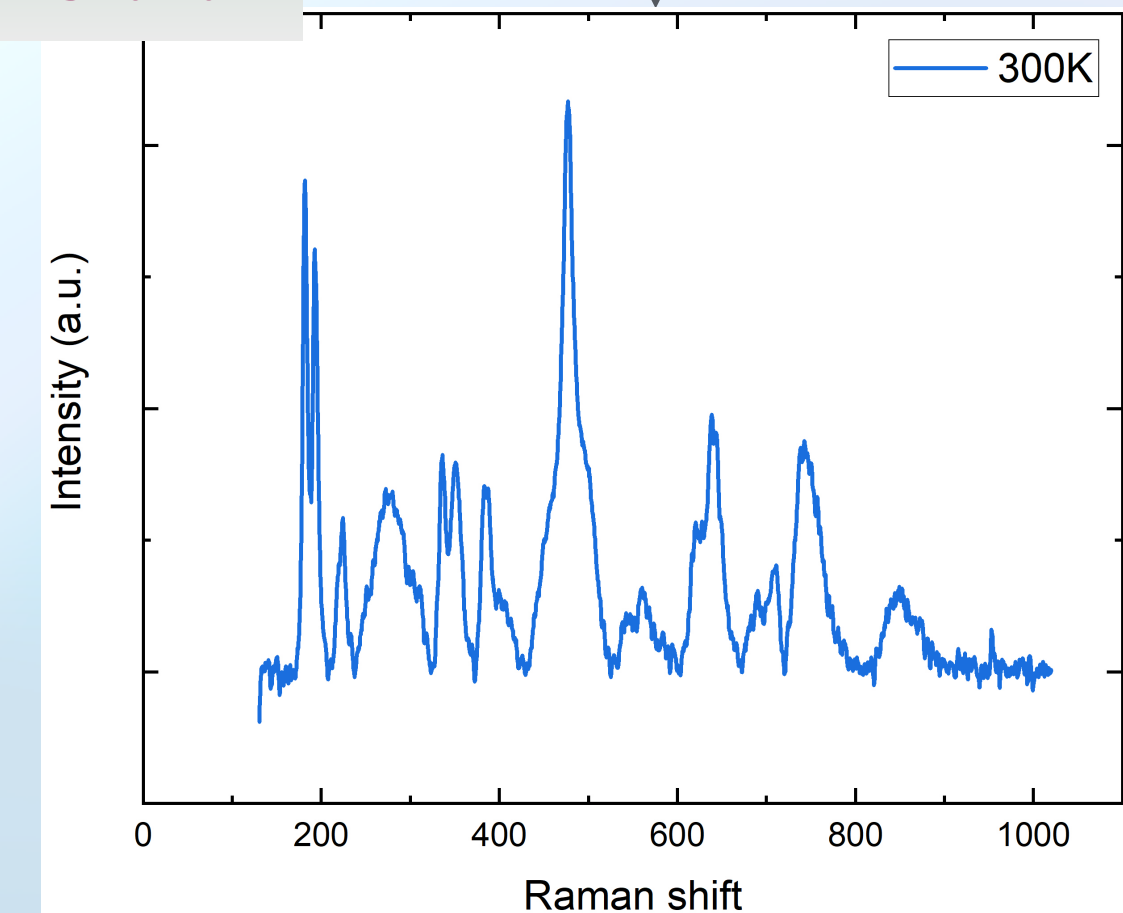
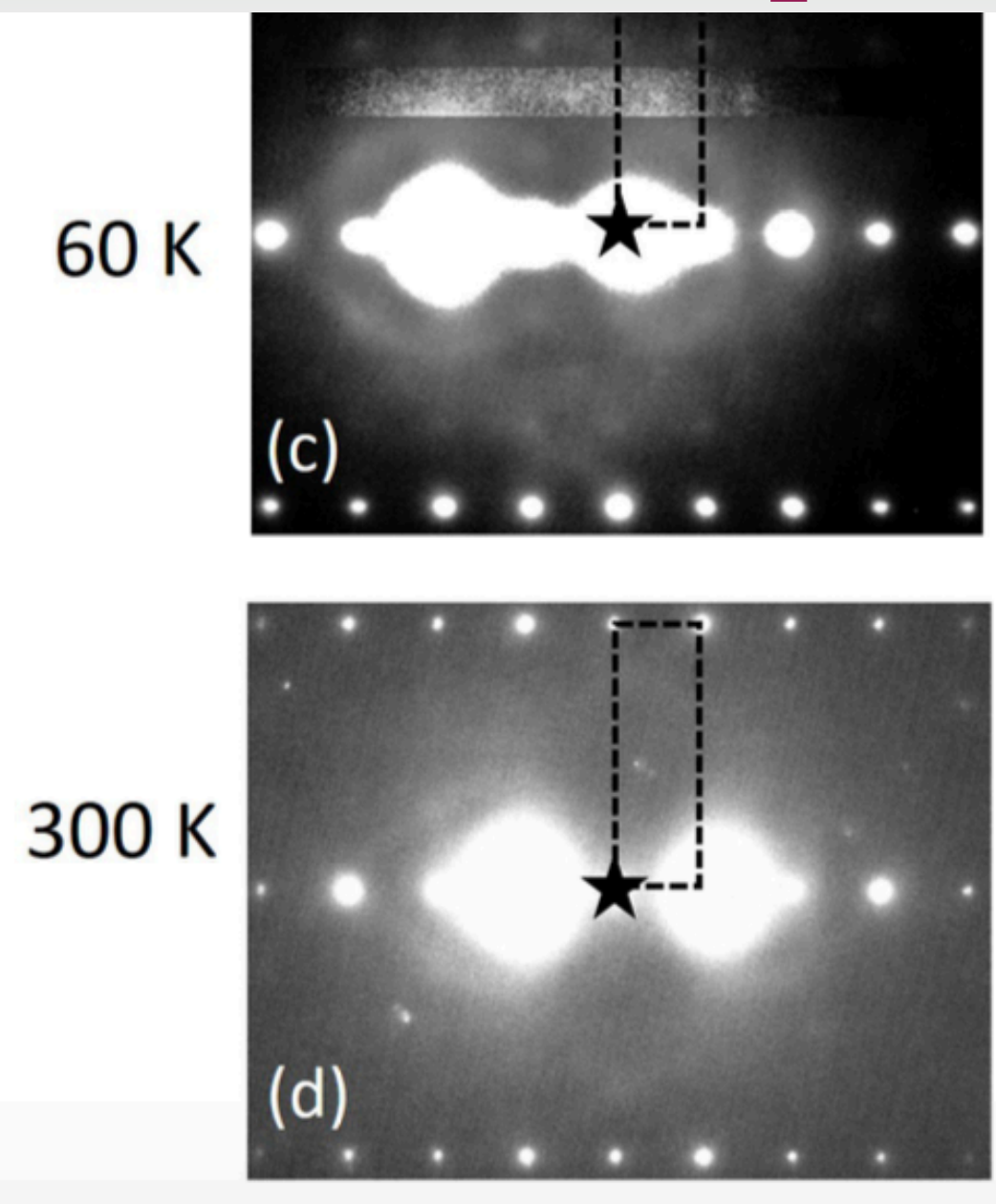
No Raman Active modes

Why strong Raman modes at room temperature??



In summary, we find that the whole Raman spectrum of BaZrO₃ can be explained by second-order Raman scattering. We do not find that the phonons at the *R*-point, where BaZrO₃ has its structural instability, play a special role. In particular, we find no evidence for scattering directly related to octahedra tilts, and no direct support for the hypothesis of distorted nanodomains.

In summary, we have provided measurements of the Raman spectrum of BaZrO₃ single crystals in a wide temperature range, and analyzed it in the light of comprehensive lattice dynamical calculations of BaZrO₃ in its cubic phase as well as in its distorted phases with octahedra tilts. We clearly identified a major contribution from second-order Raman scattering, especially overtones of the octahedra breathing modes at high frequencies. Other salient features of the Raman spectrum have also been tentatively assigned to overtones and modes

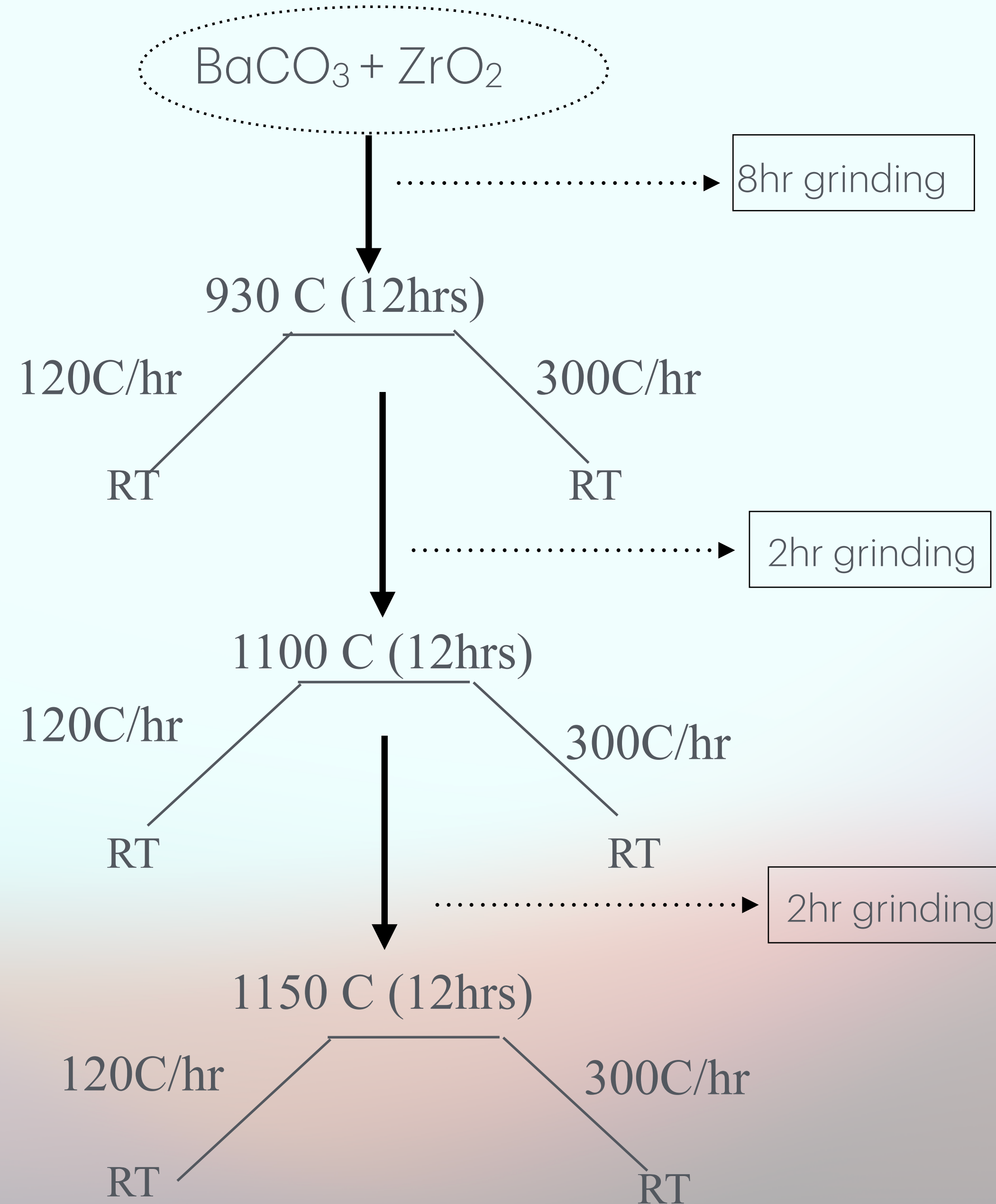


C.Tolouse, et.al, *Phys. Rev. B* **100**, 134102 (2019)

I.Levin, et.al, *Phys.Rev.B* **104**, 214109 (2021)

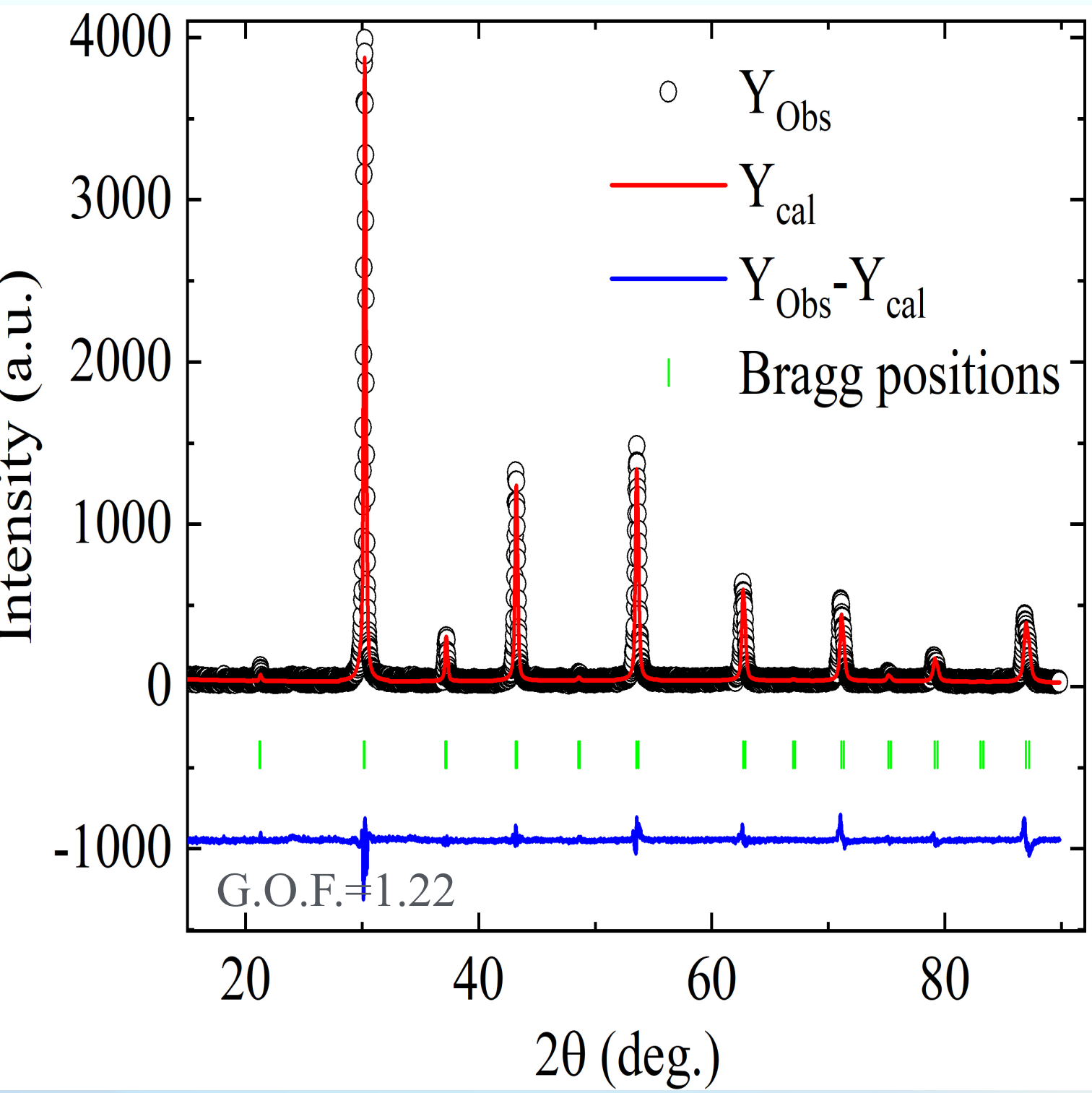
2. Synthesis Mechanism

Solid-State Route



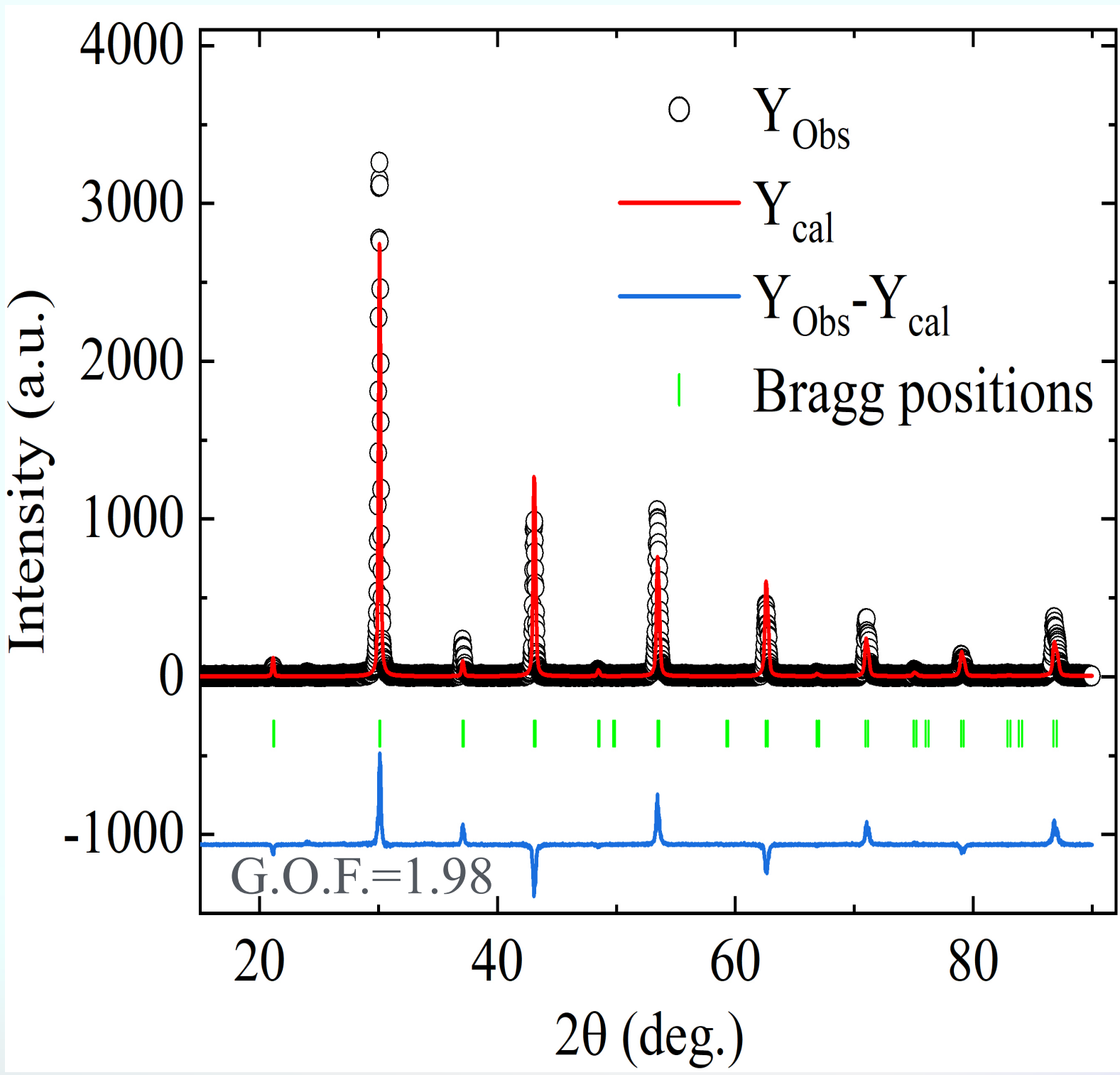
3. Results & discussions

a. Structural Characterization (XRD)



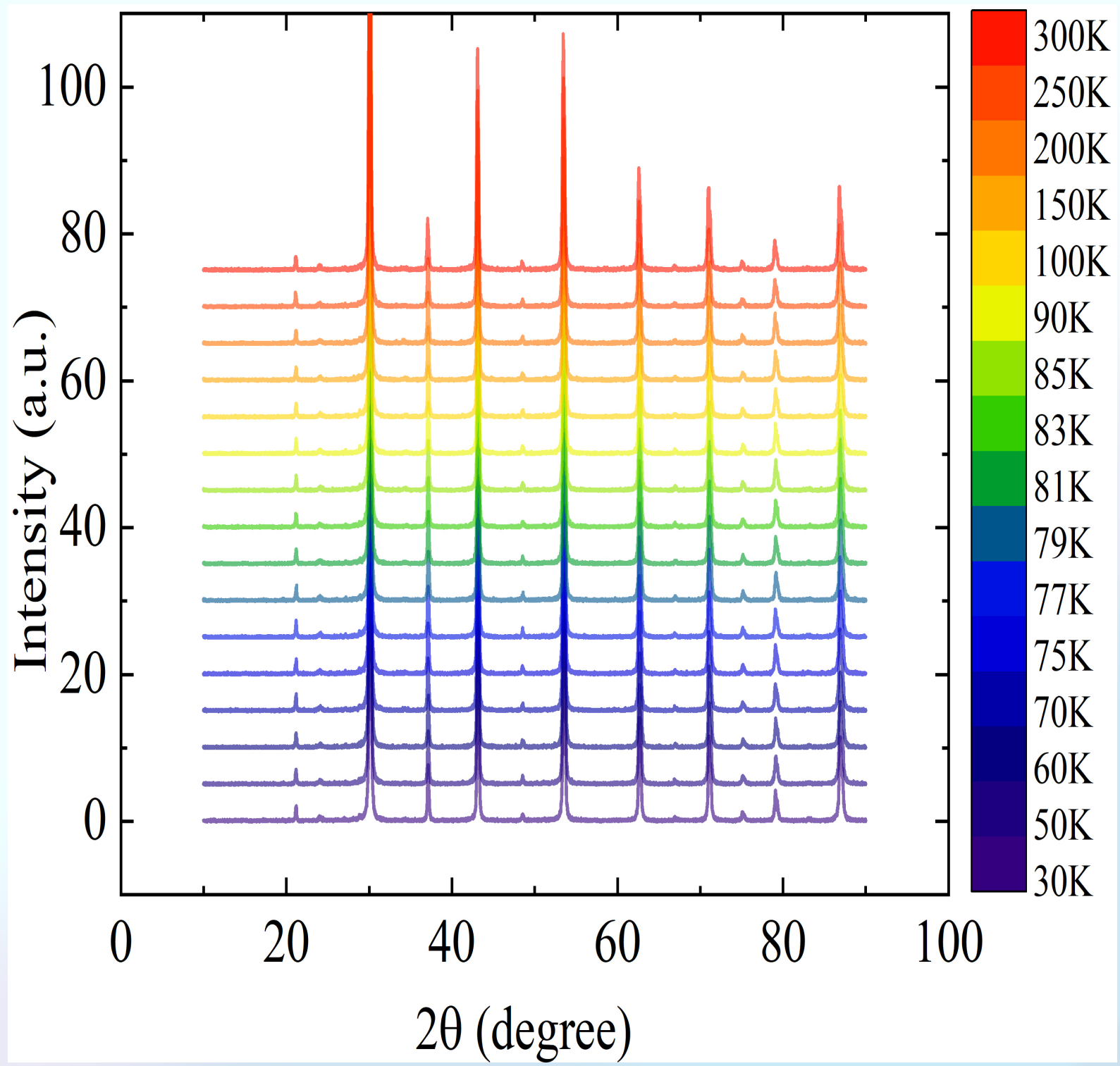
Cubic Phase space

$Pm\bar{3}m$



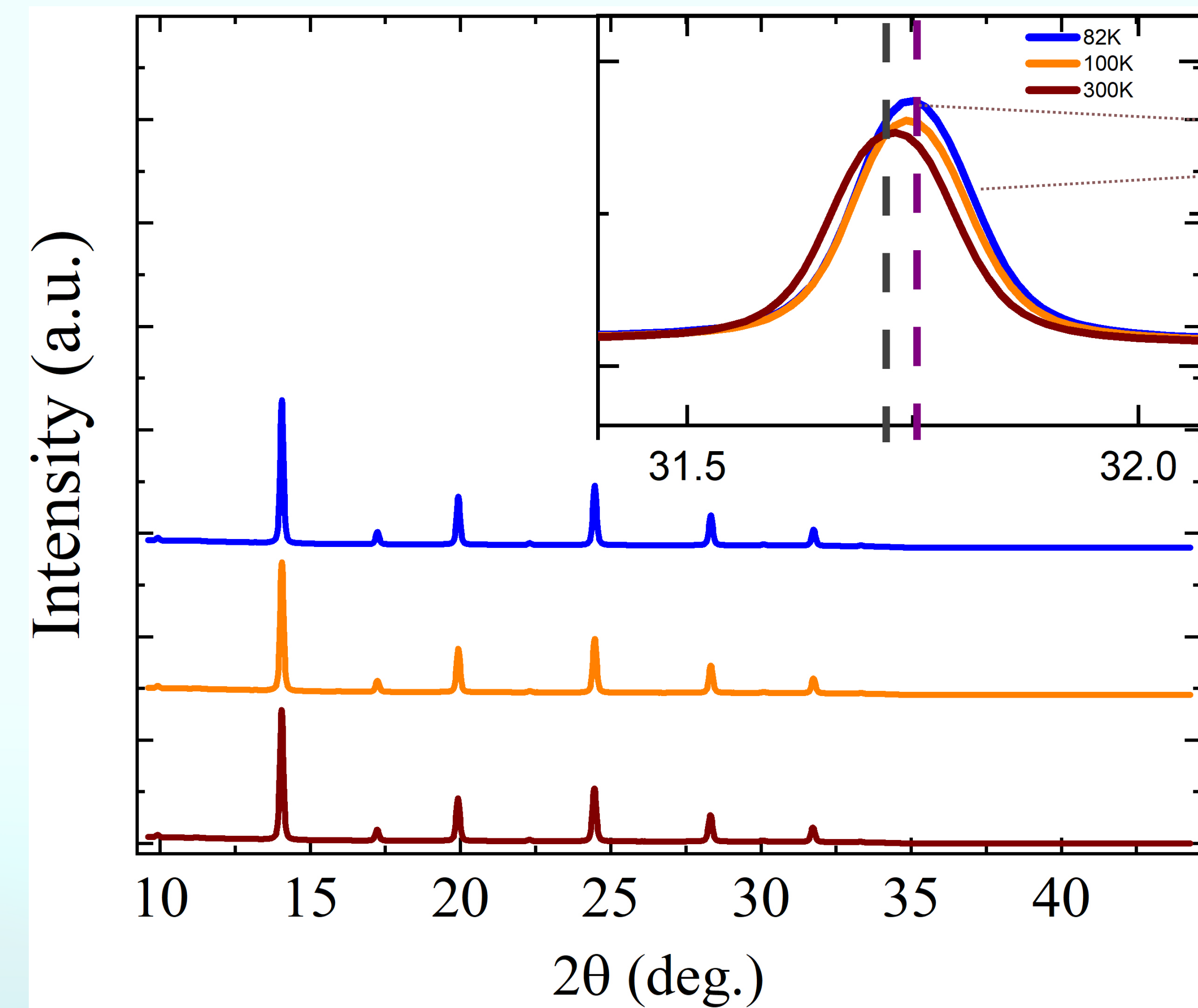
Tetragonal Phase space

$I4/mcm$



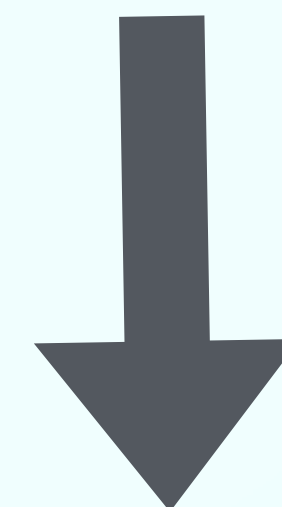
XRD doesn't show any changes in long range order

Maintained its cubic symmetry with temperature



asymmetry introducing with
lowering temperature value $\sim 80\text{K}$
(Transition temperature)

Attributed to presence of tetragonal phase at $\sim 82\text{ K}$

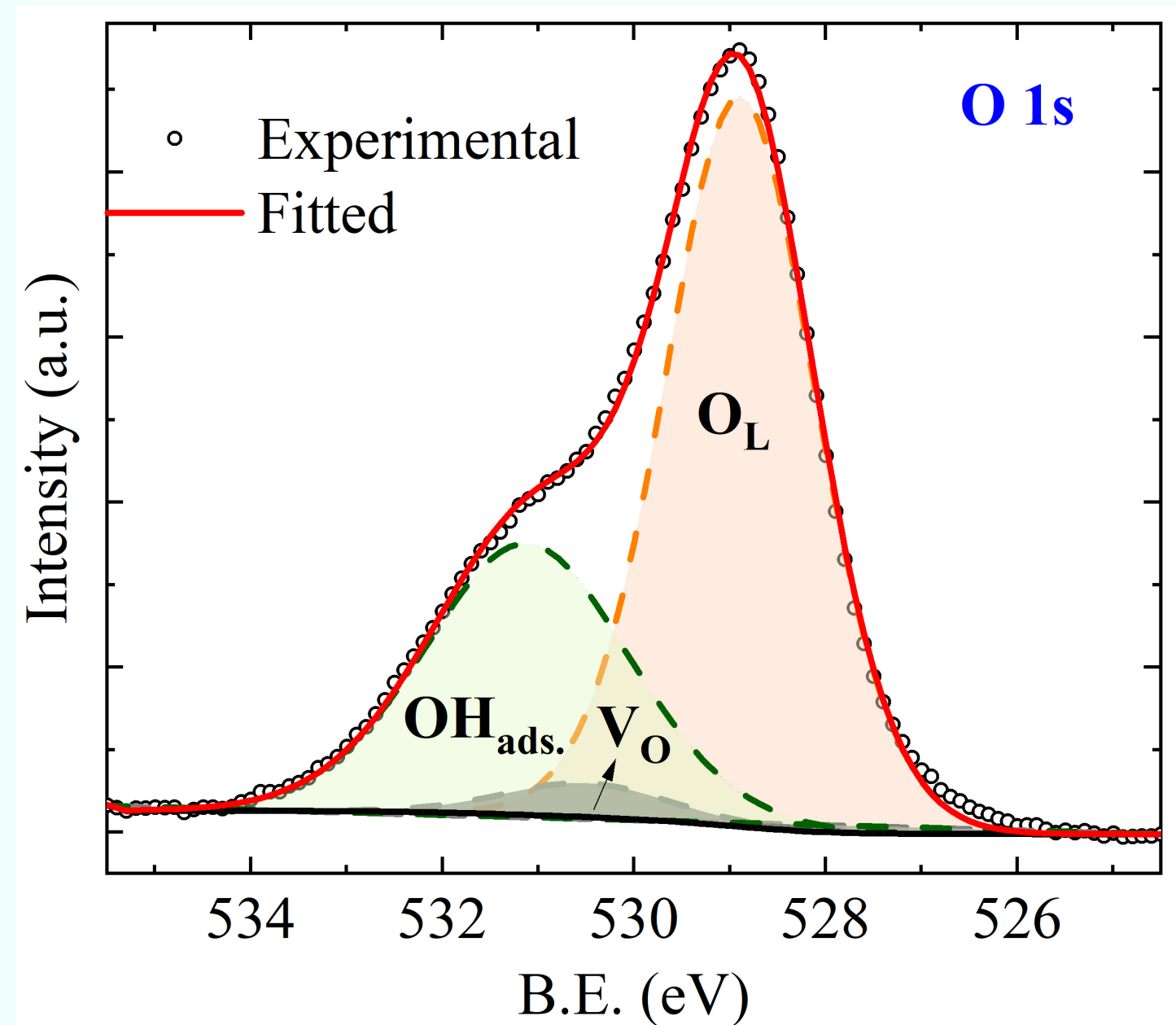
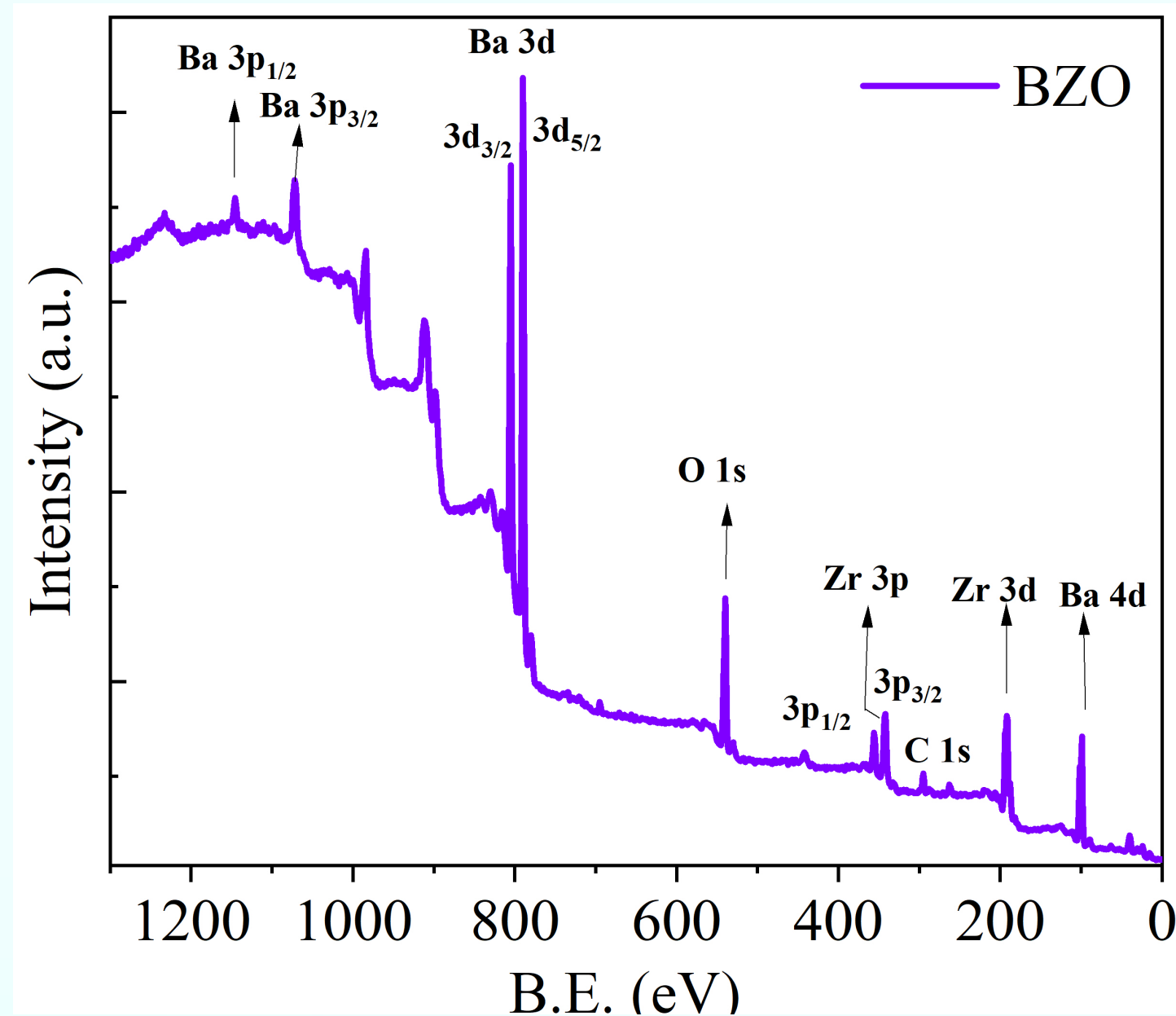


Indicating presence of Disorder

Temp-dependent Synchrotron XRD

But no tetragonal signal at room temperature!

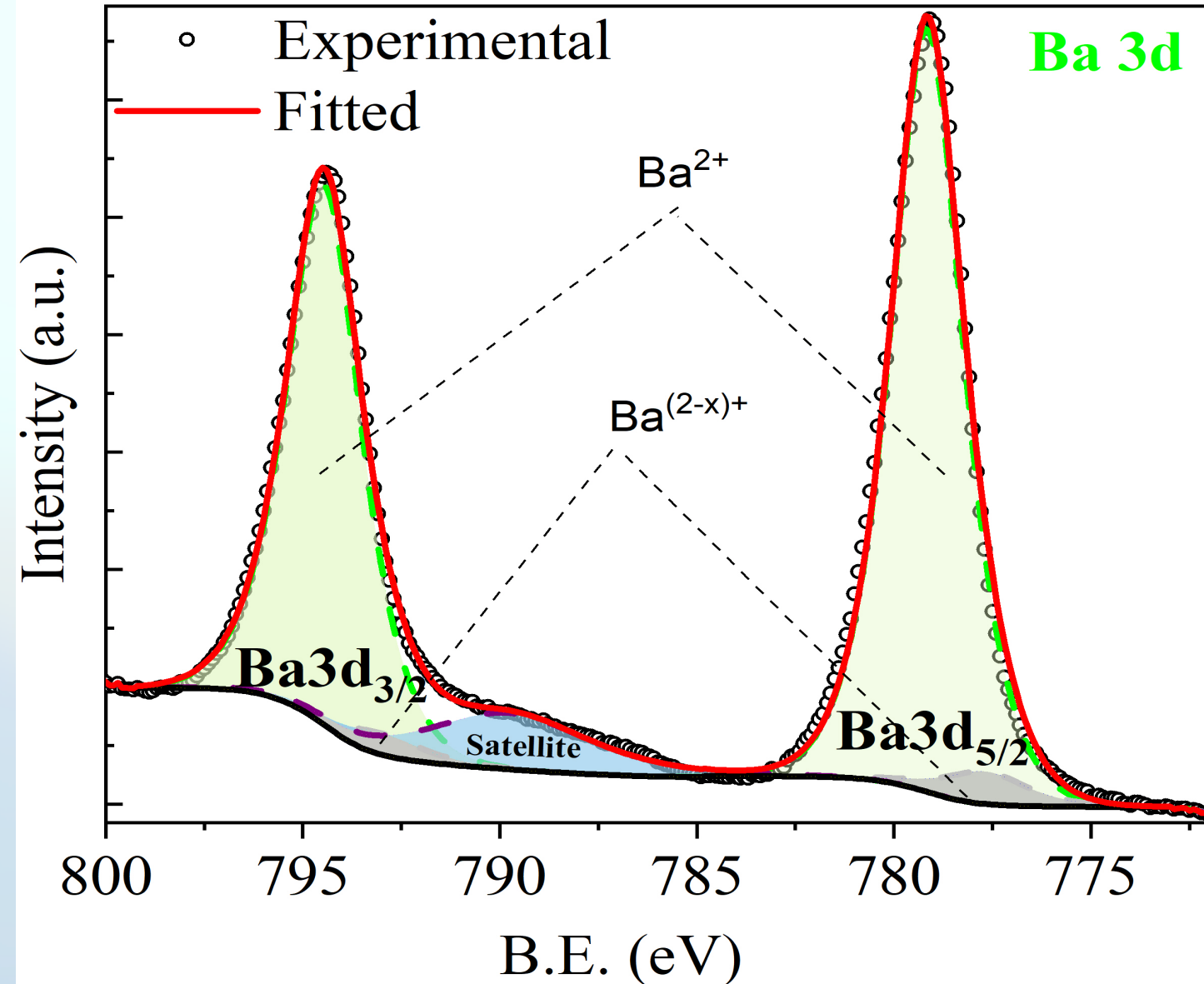
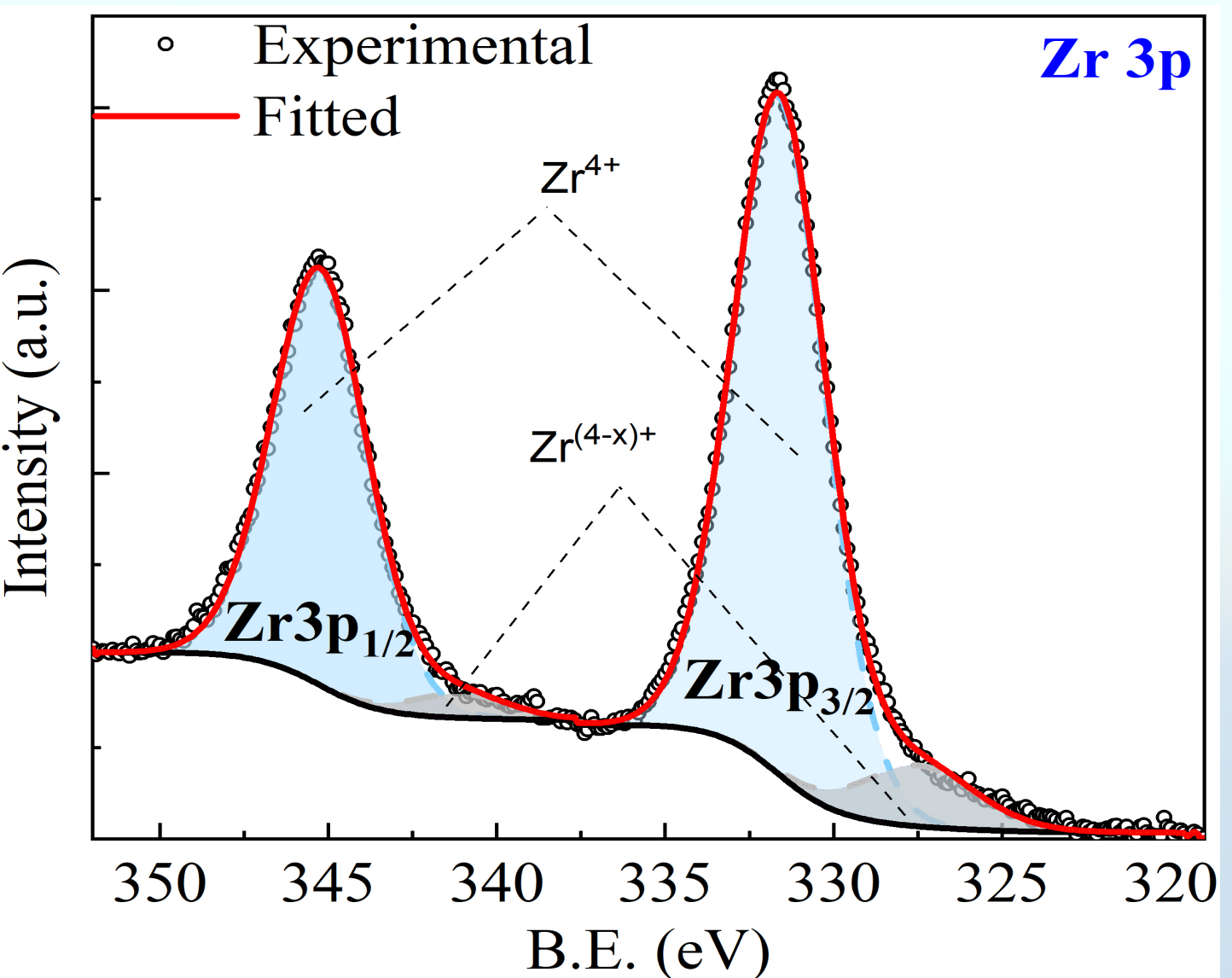
b. X-Ray Photoelectron Spectroscopy (XPS)



- Sample is in pure phase no impurity present in the BZO

O-1s XPS deconvulated in 3 peaks

- 528.9 eV corresponds to lattice oxygen O_L
- 531.2 eV corresponds to -OH group OH_{ads.}
- 530.4 eV for Oxygen vacancy V_O

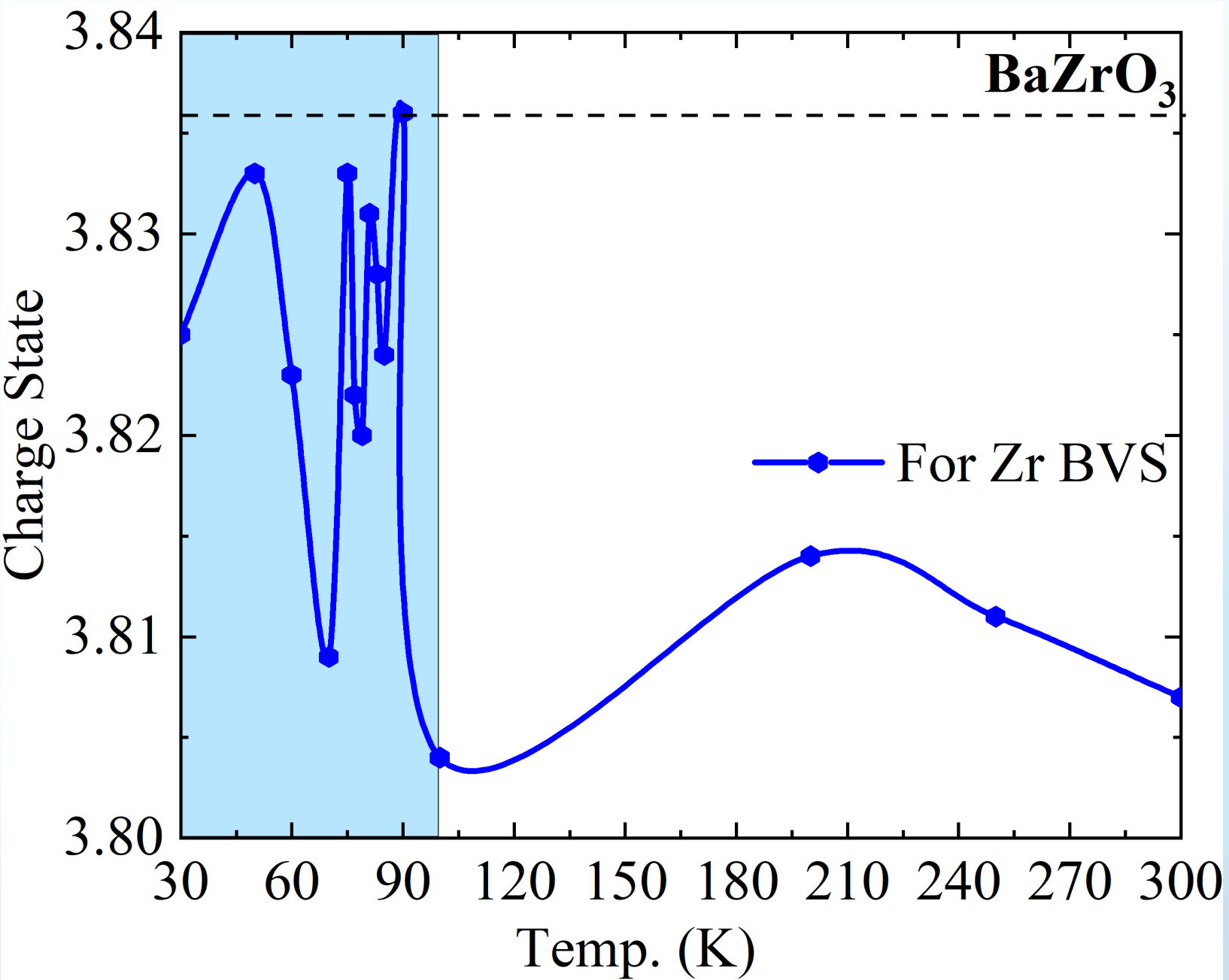
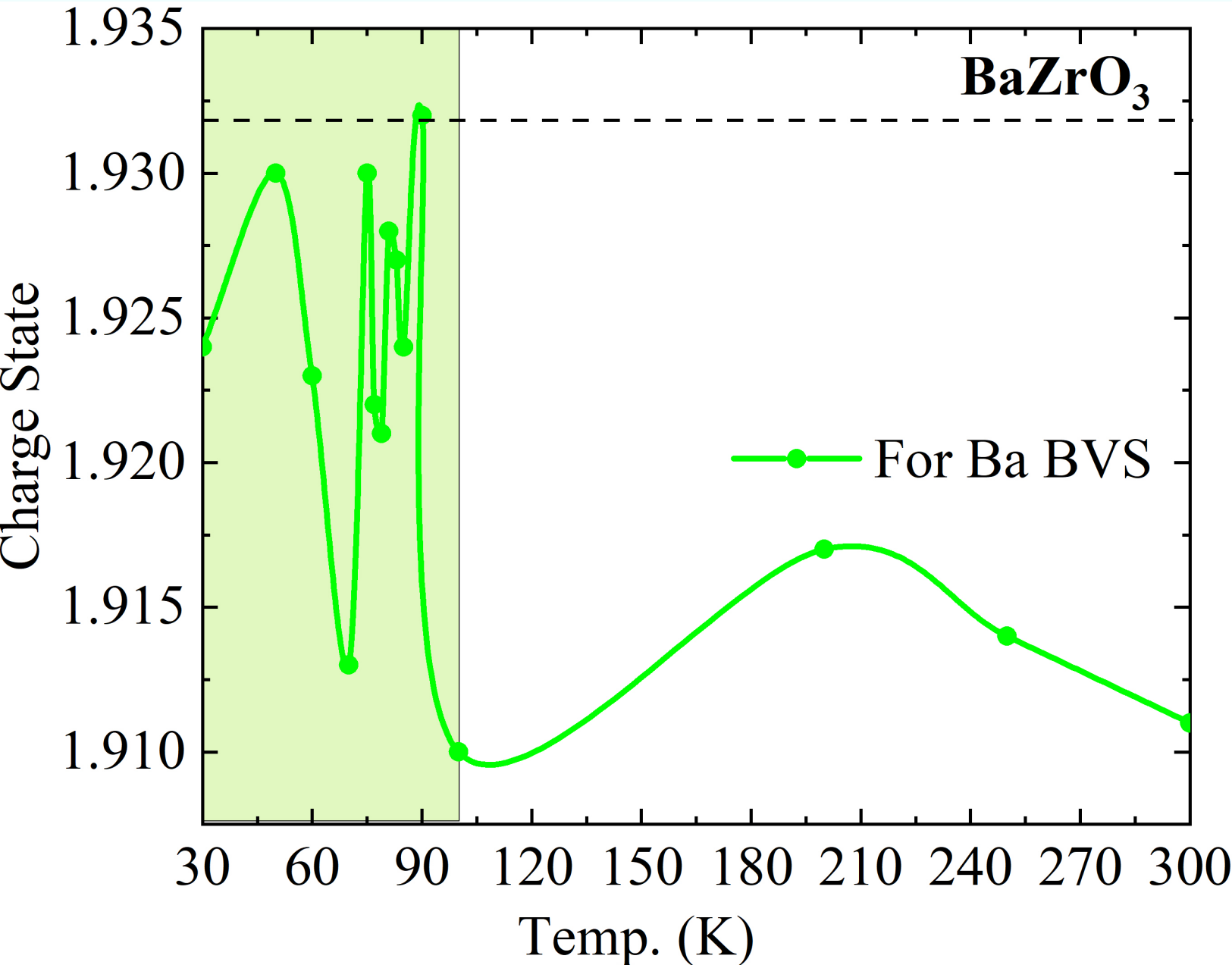
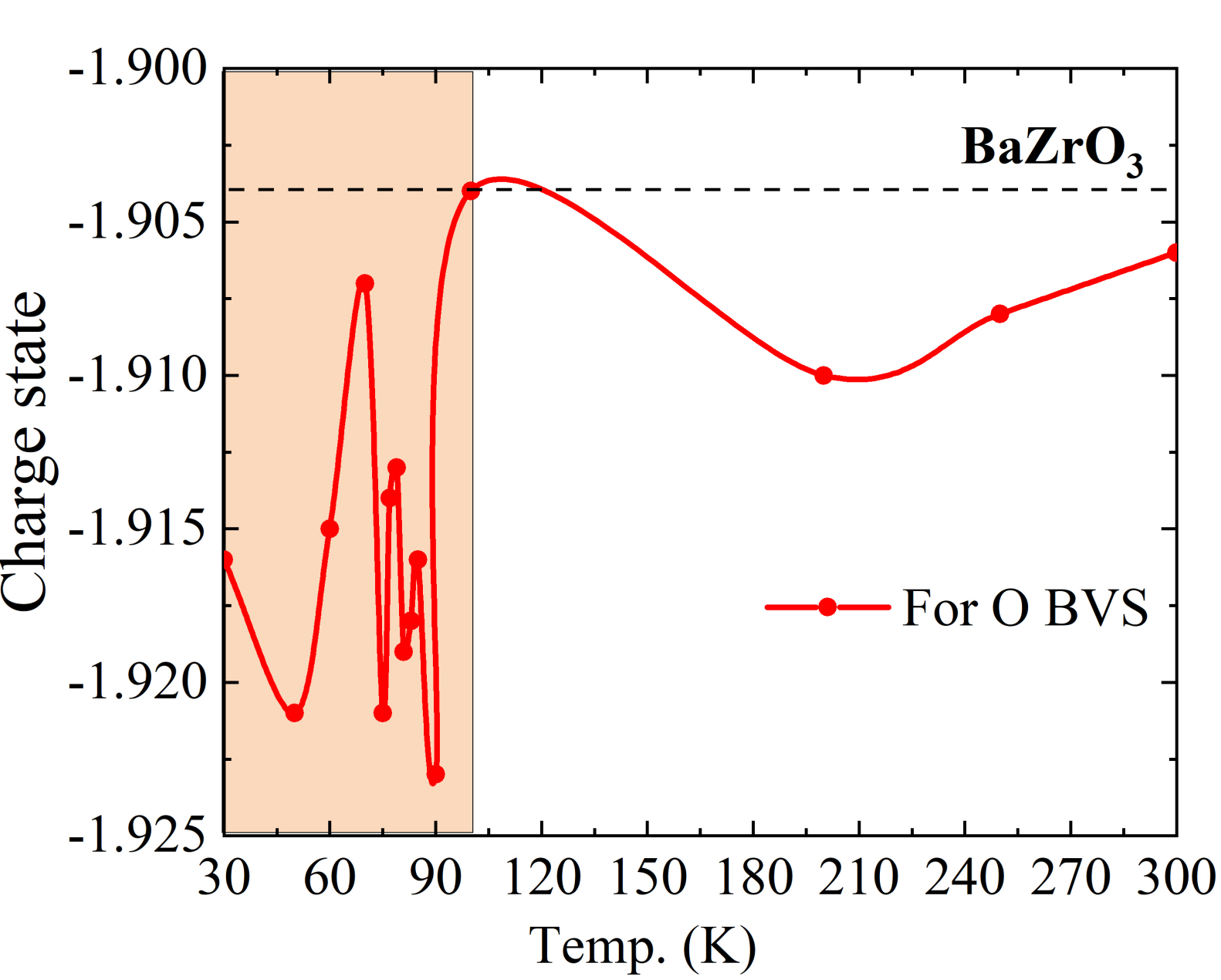


Bond-Valance Sum Analysis

$$V_i = \sum_i [\exp(d_i - d_0)]/B$$

Bond-valance

Empirical constant=0.37



BVS analysis with temperature variation shows that charge state of lattice oxygen is ~ -1.92 instead of -2 , confirms the partial absence of stoichiometric lattice oxygen in BZO system resulted in Ba and Zr atom

Vacancy formation: DFT & aiT

What's happening at atomistic level??

Any role of defects??

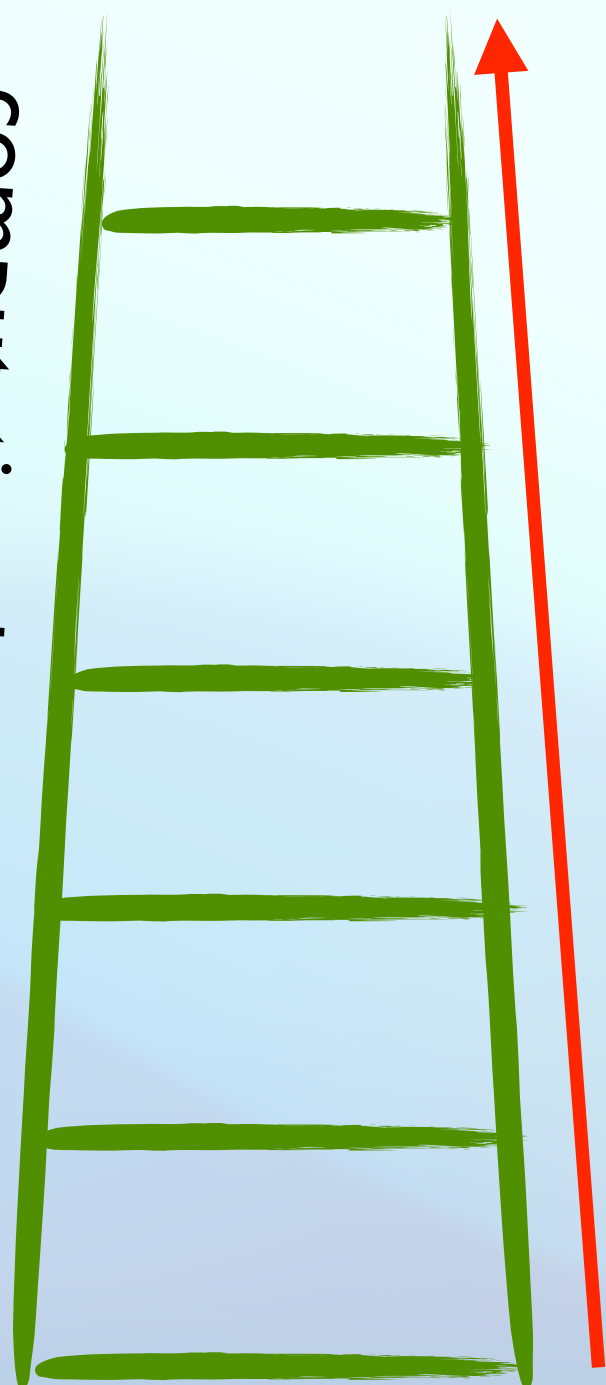
....successive refinement of ψ



$$H\psi = E\psi$$

“Towards Heaven”
ie. exact solution

computational cost, accuracy



many body terms:
RPA, GW



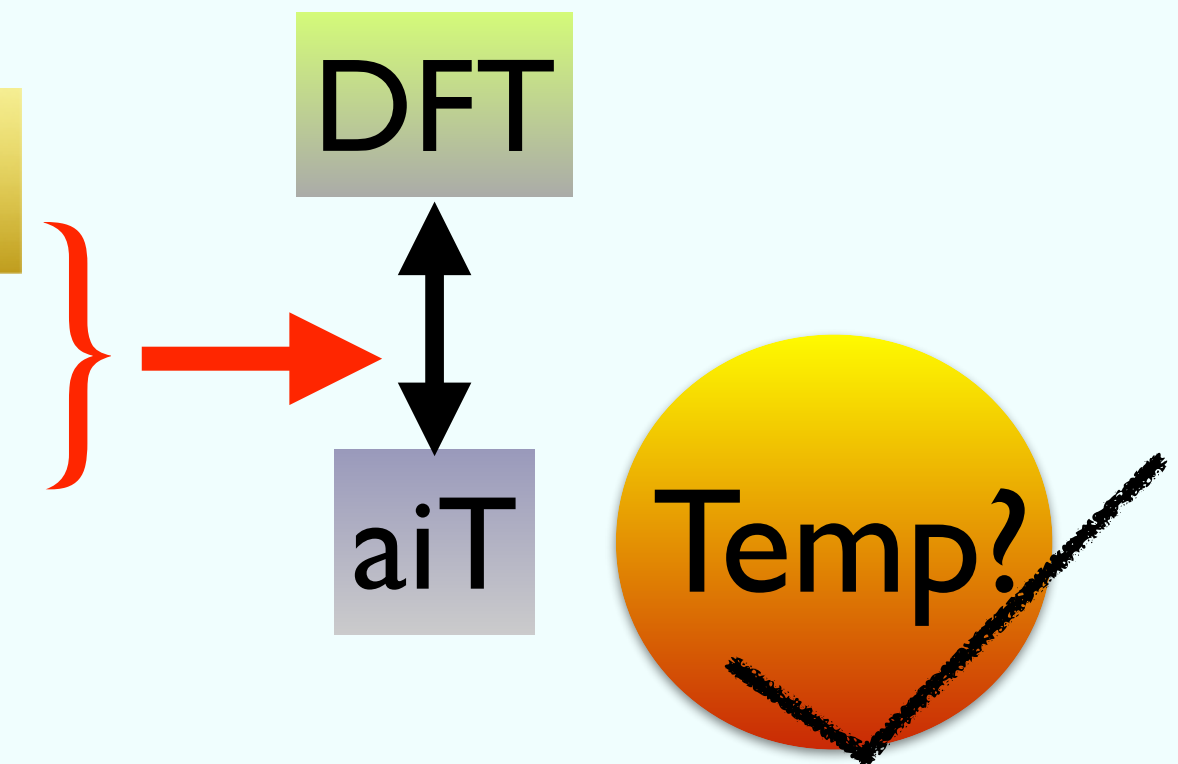
Walter Kohn
Nobel Prize Oct. 1998

hybrid functionals: non-local exchange

meta-GGA: $\nabla^2 n(r), \nabla^2 \phi(r)$

Generalized gradient approximation (GGA): $|\nabla n(r)|$

Local-density approximation (LDA): $n(r)$



Density functional theory

(Hohenberg-Kohn 1964, Kohn-Sham 1965)
Phys. Rev. **136**, B864 (1964), Phys. Rev. **140**, A1133 (1965)

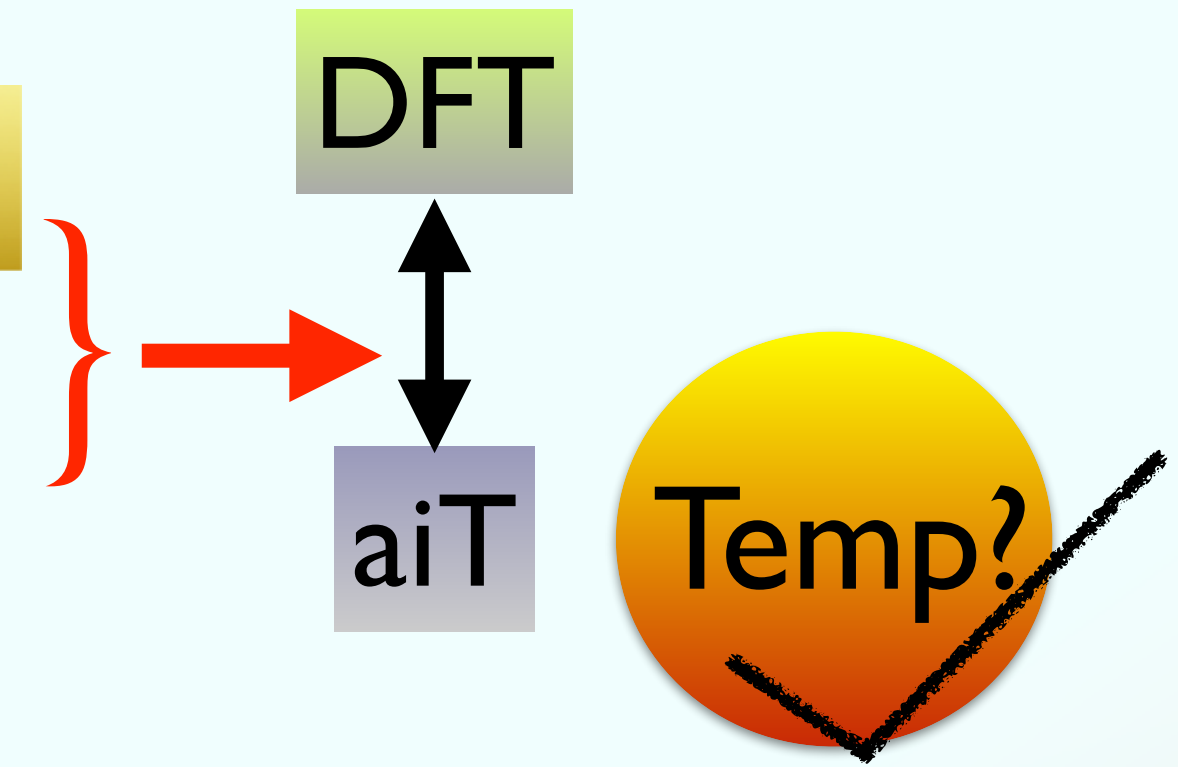
$$E_{\text{tot}} = E[n(r)] = T_s[n] + V[n] + V_{\text{es}}[n] + E_{\text{xc}}[n]$$

Challenge is to find the proper E_{xc} .

Vacancy formation: DFT & aiT

What's happening at atomistic level??

Any role of defects??



Formation Energy of Neutral Vacancy:

$$\Delta E_{form} = E(Ba_n Zr_n O_{3n-1}) - E(Ba_n Zr_n O_{3n}) + \mu_O$$

Formation Energy of Charged Vacancy:

$$\Delta E_{form} = E(Ba_n Zr_n O_{3n-1}) - E(Ba_n Zr_n O_{3n}) + \mu_O + q \times (\mu_e + \Delta V)$$

Gibb's Free Energy:

$$\Delta G_{form}(T, p) = \Delta E_{form} + \frac{1}{2} \mu_{O_2}(T, p)$$

μ_o = chemical potential of the defected atom

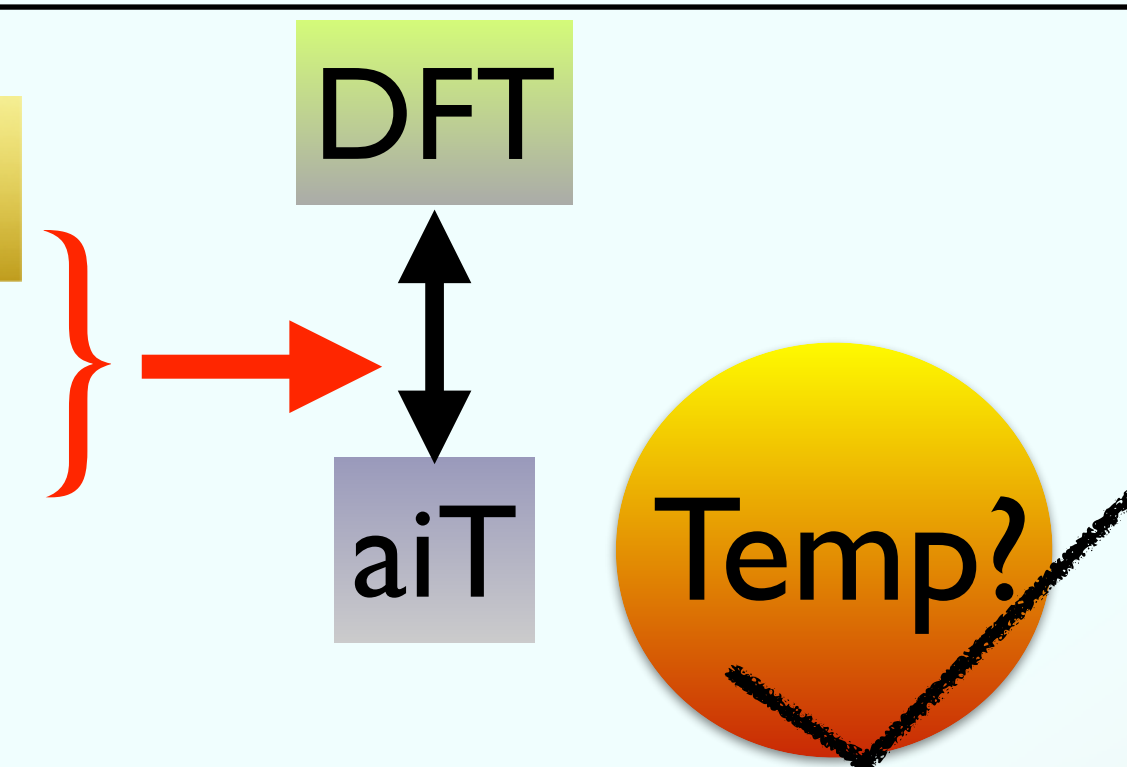
μ_e = chemical potential of the electron; ΔV = shift in core level

JANAF Thermodynamic Table

Vacancy formation: DFT & aiT

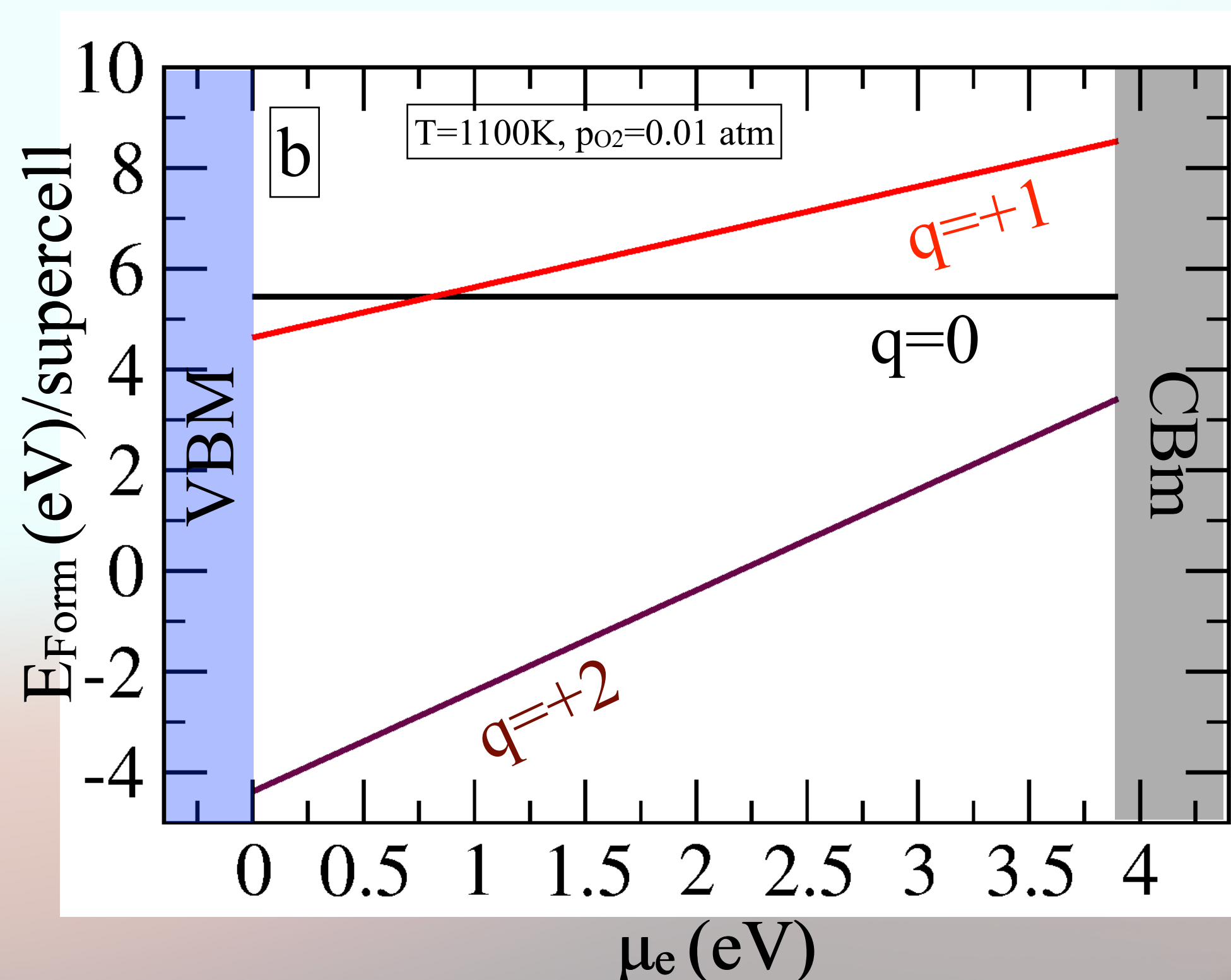
What's happening at atomistic level??

Any role of defects??



DFT Calculation details:

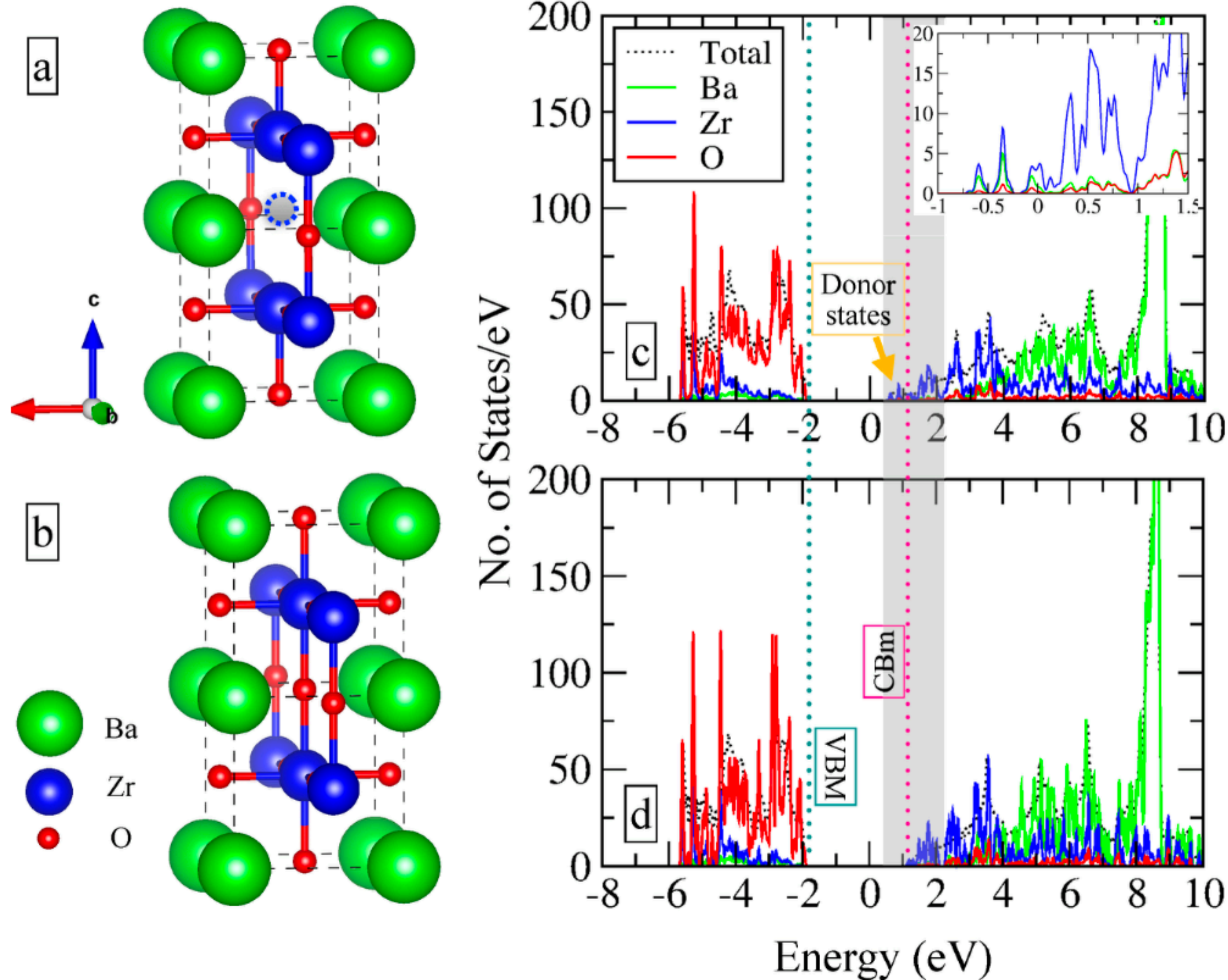
- 📌 All electron calculation
- 📌 fhi-aims code¹
- 📌 GGA calculation with PBE²
- 📌 Validated with hybrid functional calculation



1. V Blum et al. Comput. Phys. Commun. **180**, 2175 (2009).

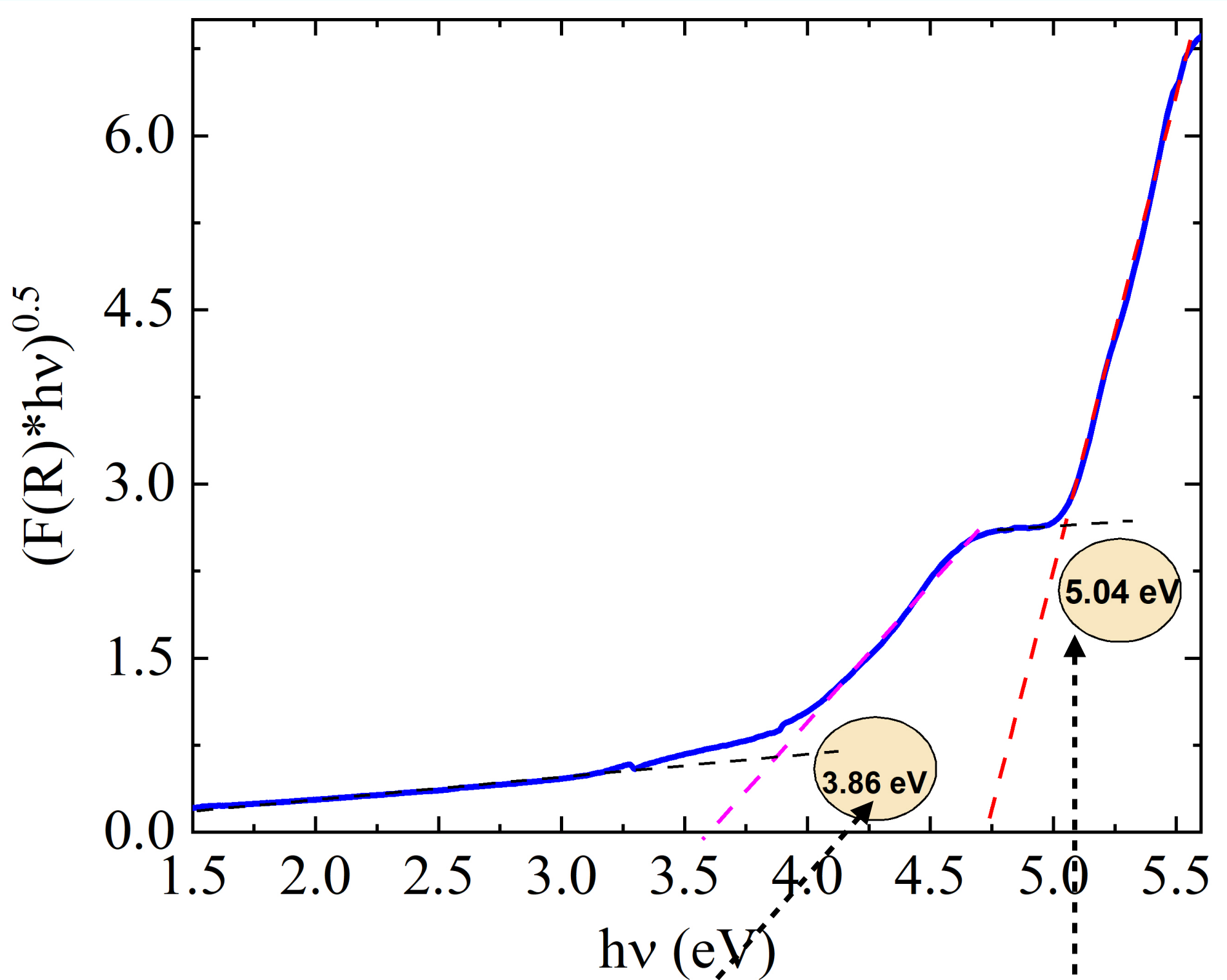
2. J P Perdew et al., Phys. Rev. B. **45**, 13244 (1992).

Electronic Structure: Density of states



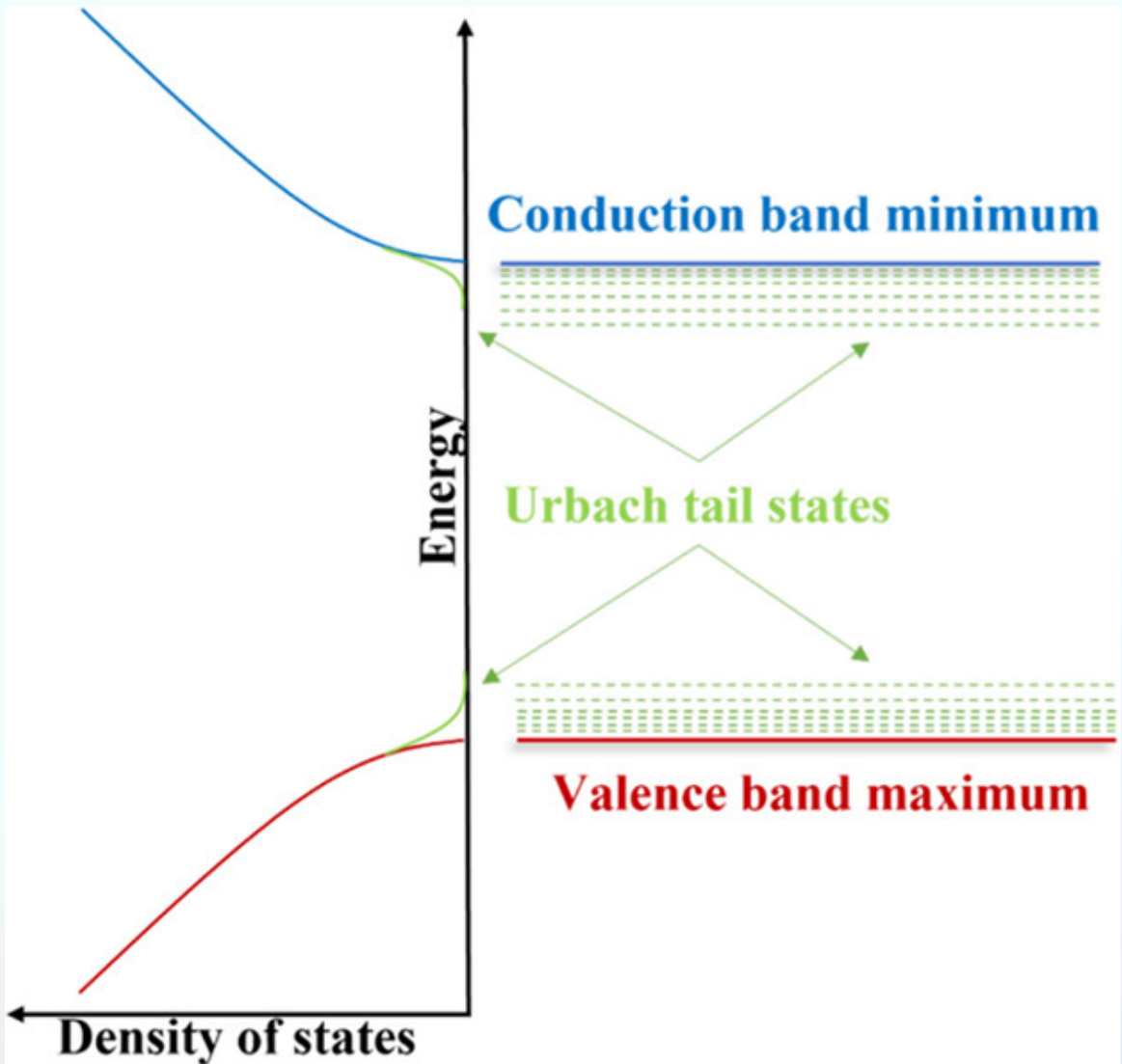
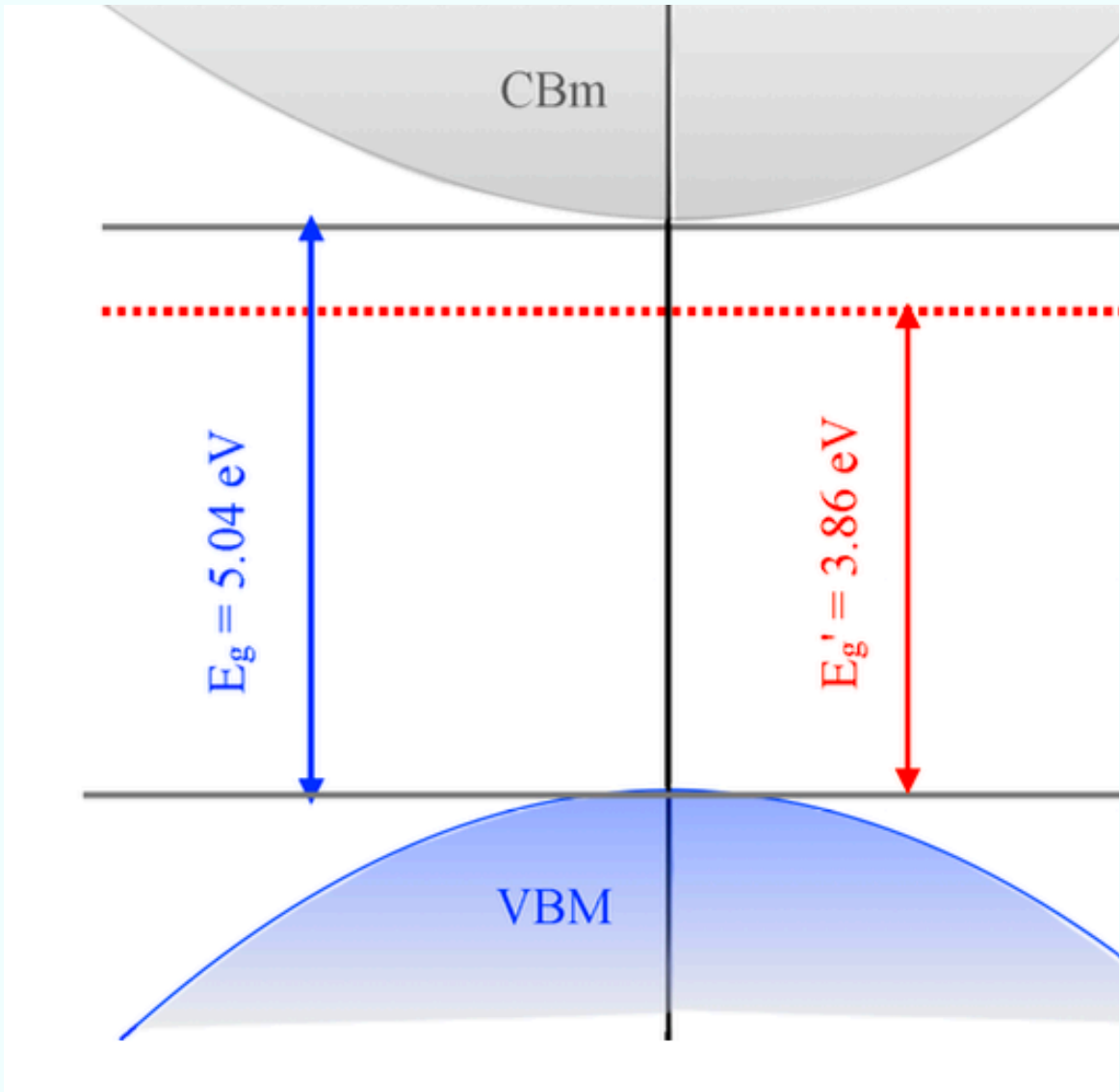
Charged Oxygen vacancy are stable confirmed by ab-initio thermodynamics calculations showing shallow donor states lies down to conduction band minima

c. UV-Vis. & FTIR Spectroscopy

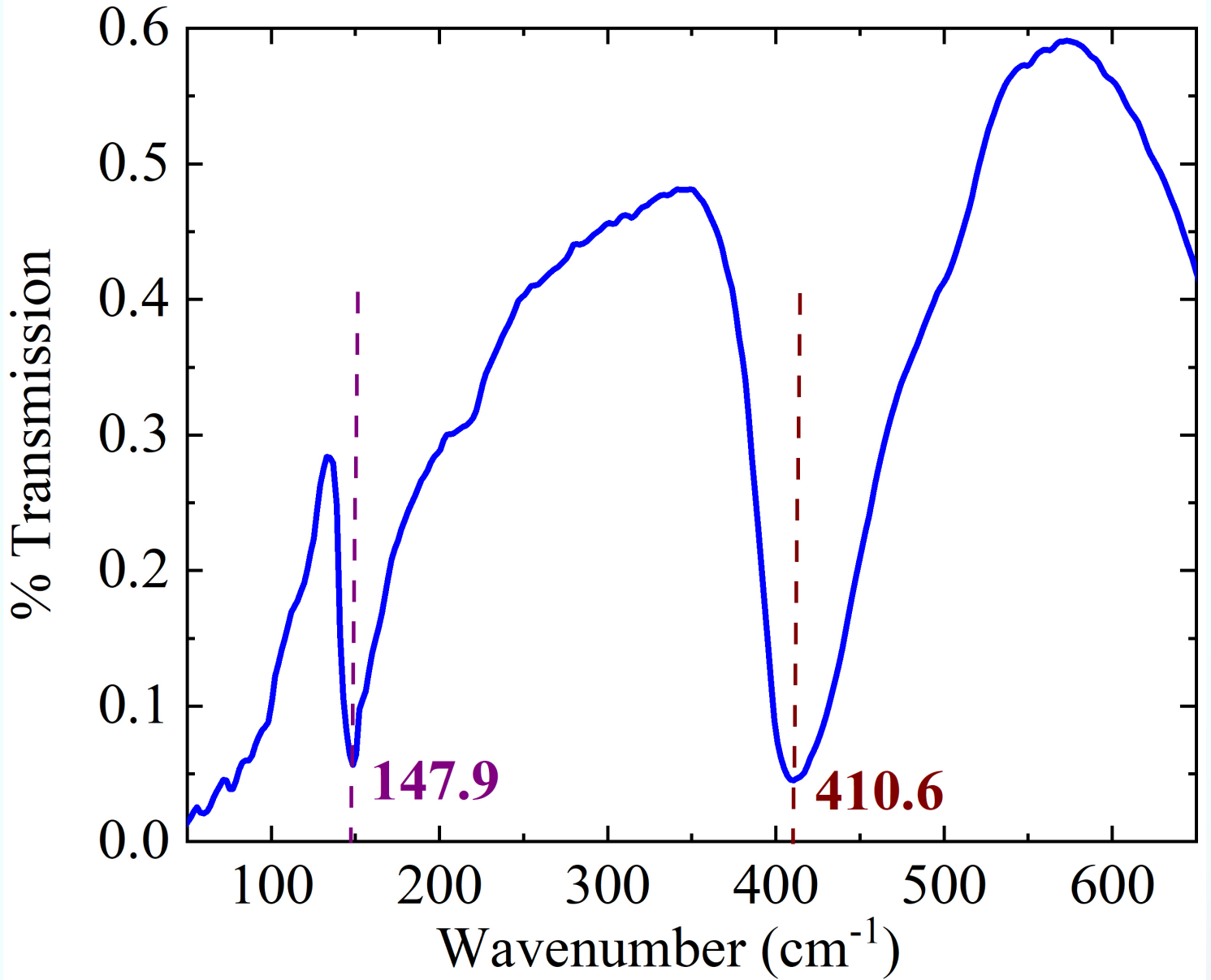


Disordered transition

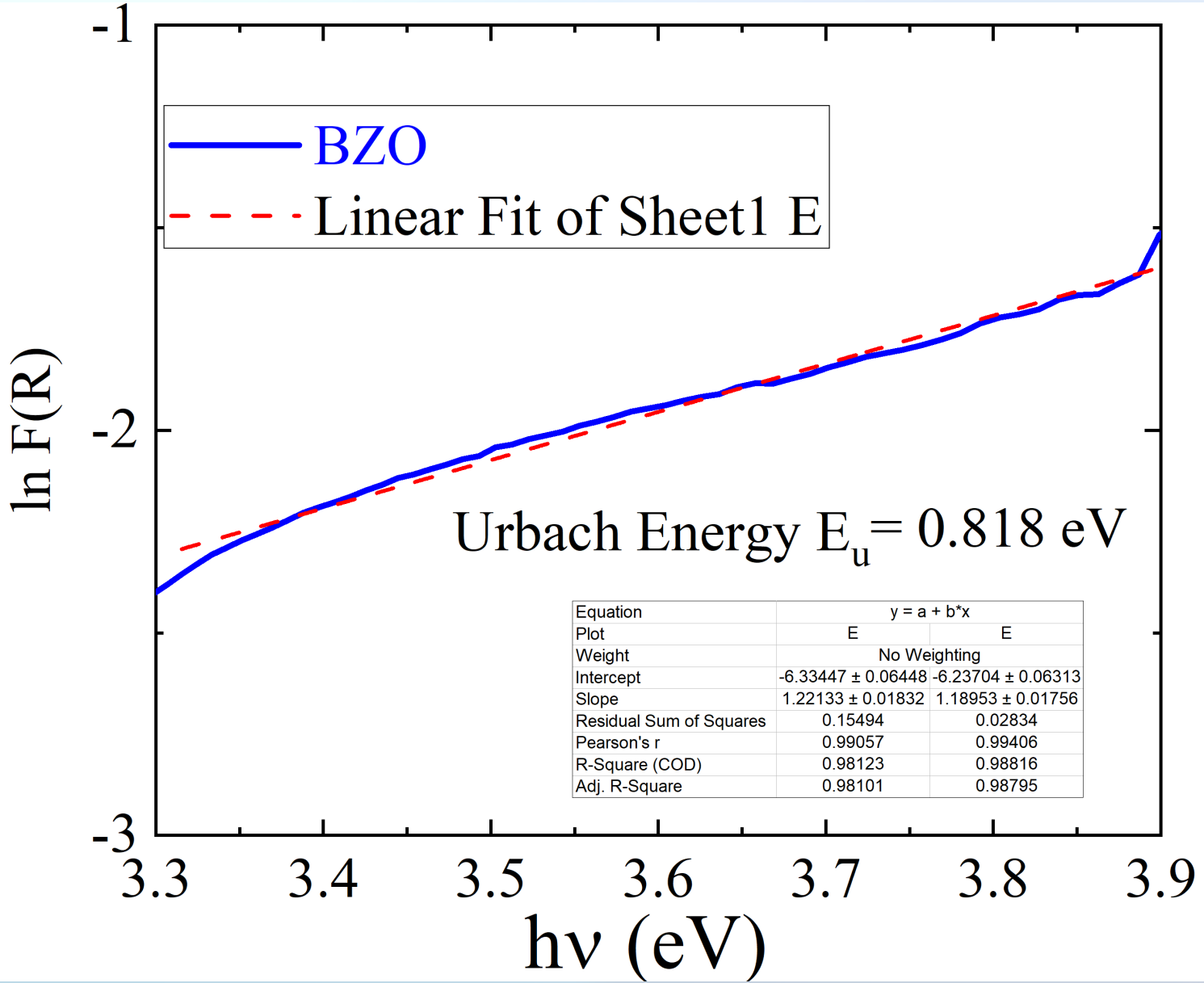
Band to band transition



E_u quantifies energetic disorder in the band edges of semiconductor

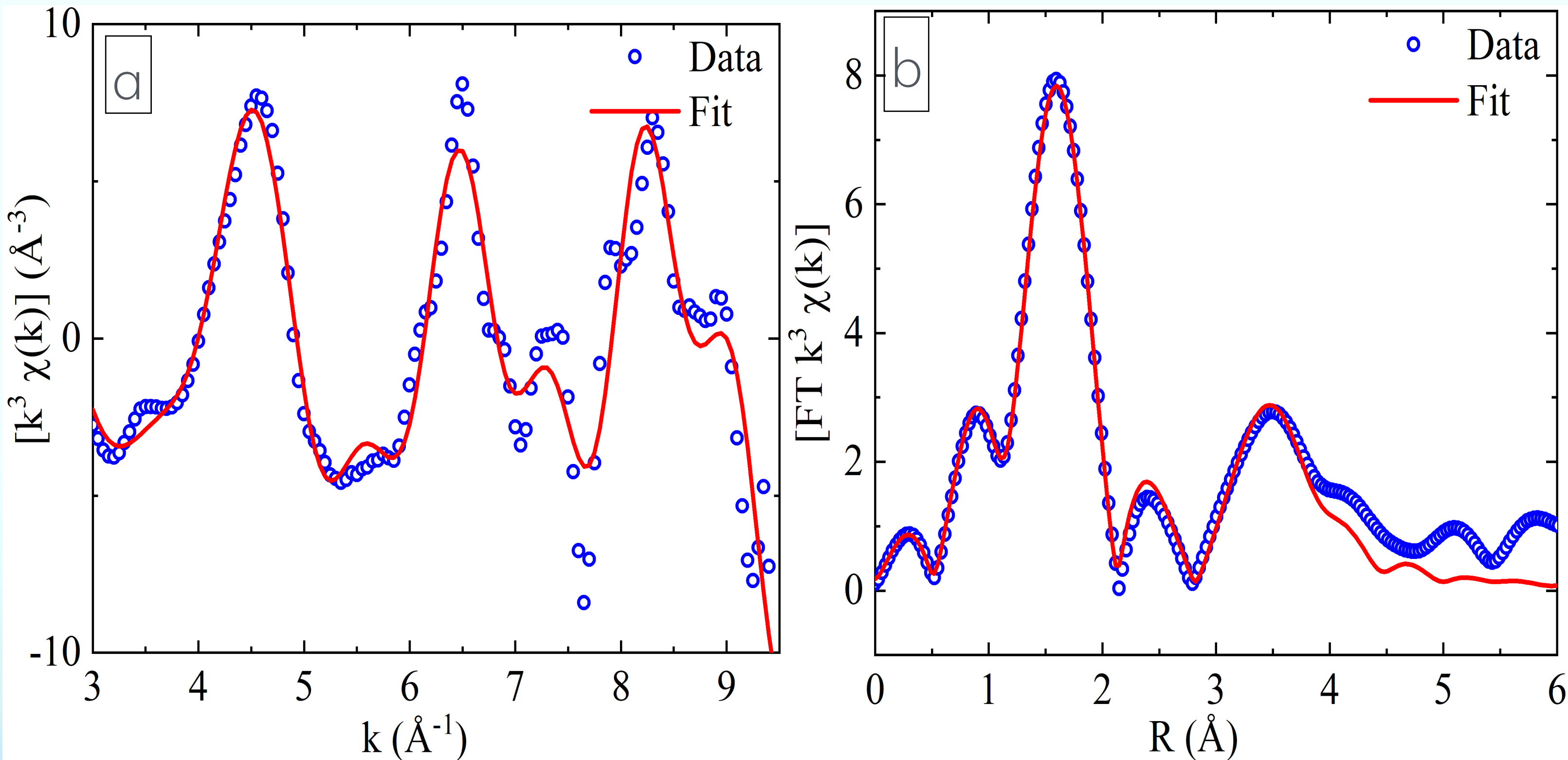


These modes ascribed to $\delta(\text{Ba} - \text{O} - \text{Zr})$ mode Characteristics of Ba-O_{12} tetrahedral groups



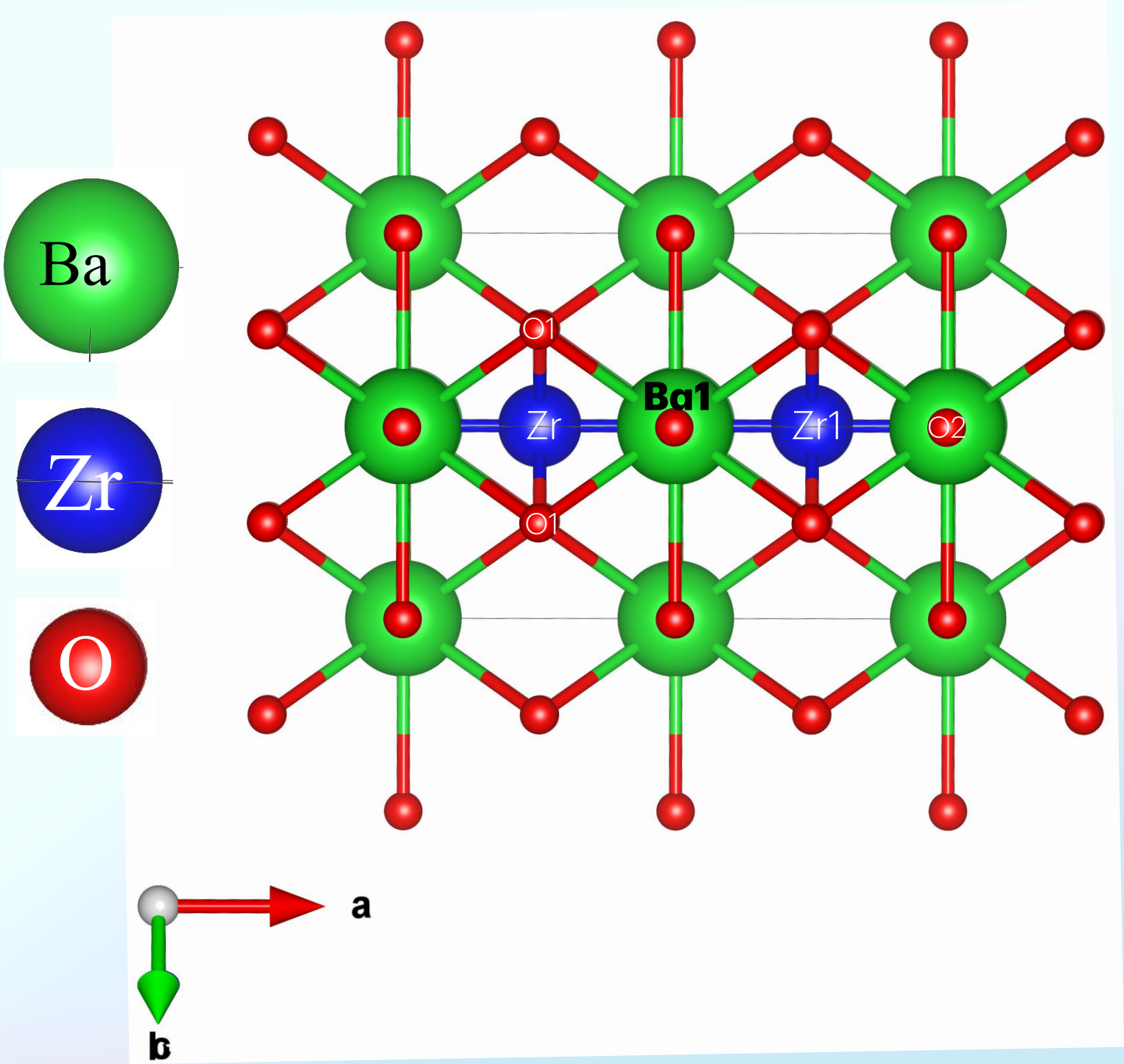
d. Extended X-Ray Absorption Fine Structure (EXAFS)

Room Temperature study

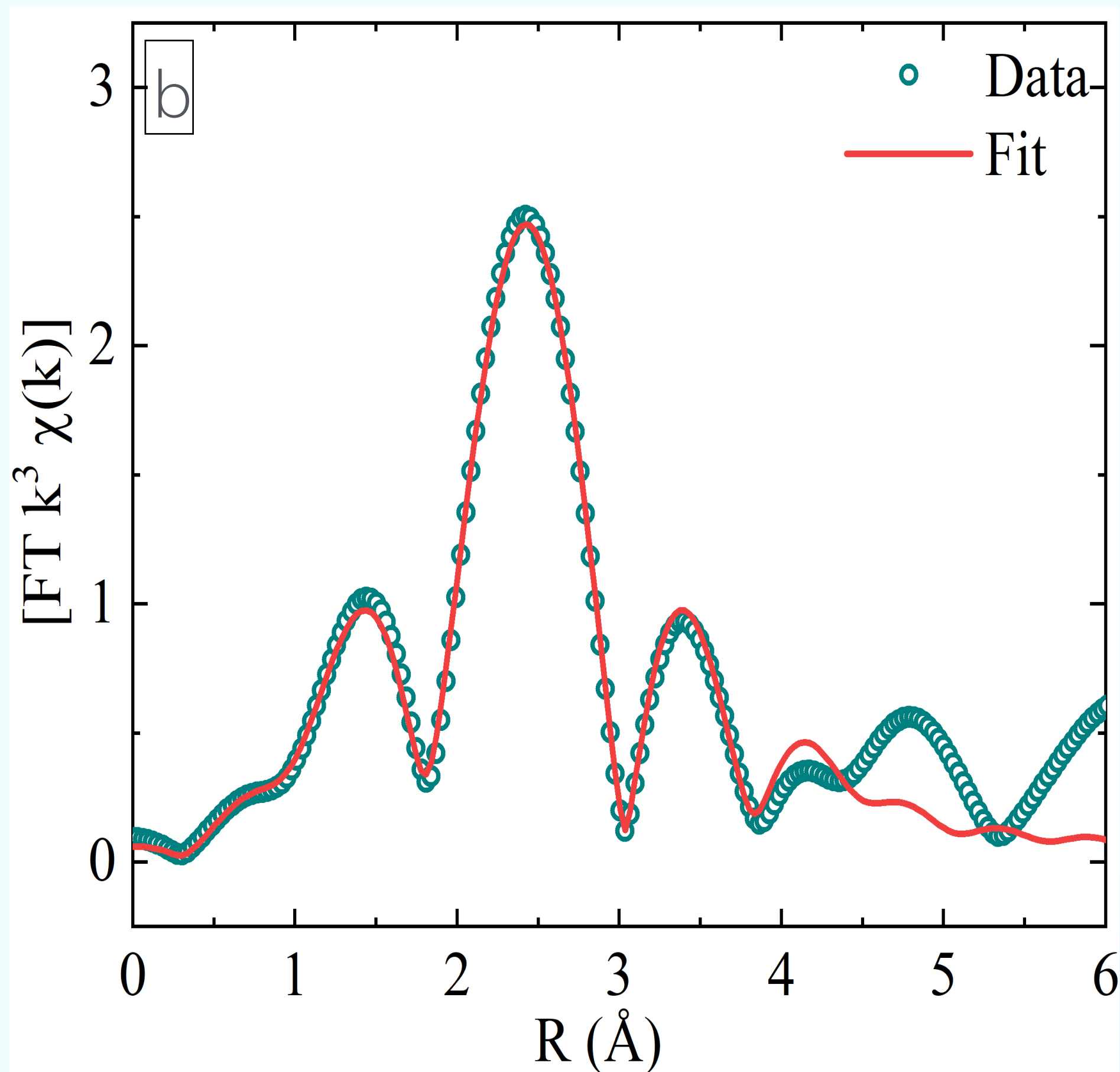
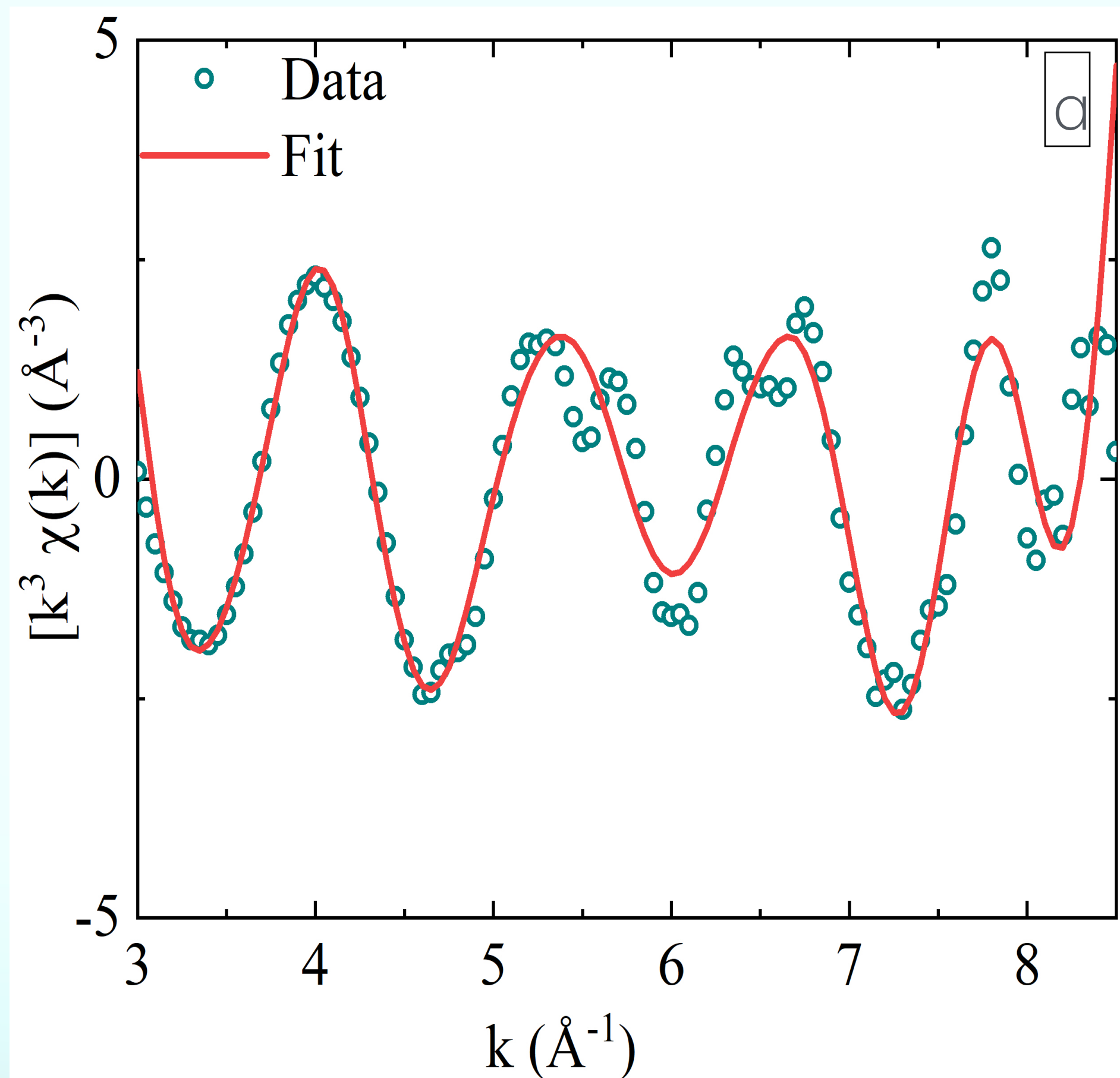


At Zr K-edge

Bond	CN	R (Å)	σ^2 (Å)	R-factor
Zr-O1	6	2.12 ± 0.005	0.006 ± 0.0008	0.021
Zr-Ba1	8	3.77 ± 0.013	0.010 ± 0.002	-
Zr-Zr1	6	4.29 ± 0.095	0.022 ± 0.016	-



Schematic presentation of 211 supershell of BaZrO₃ cubic structure for understanding of local environment around the atom

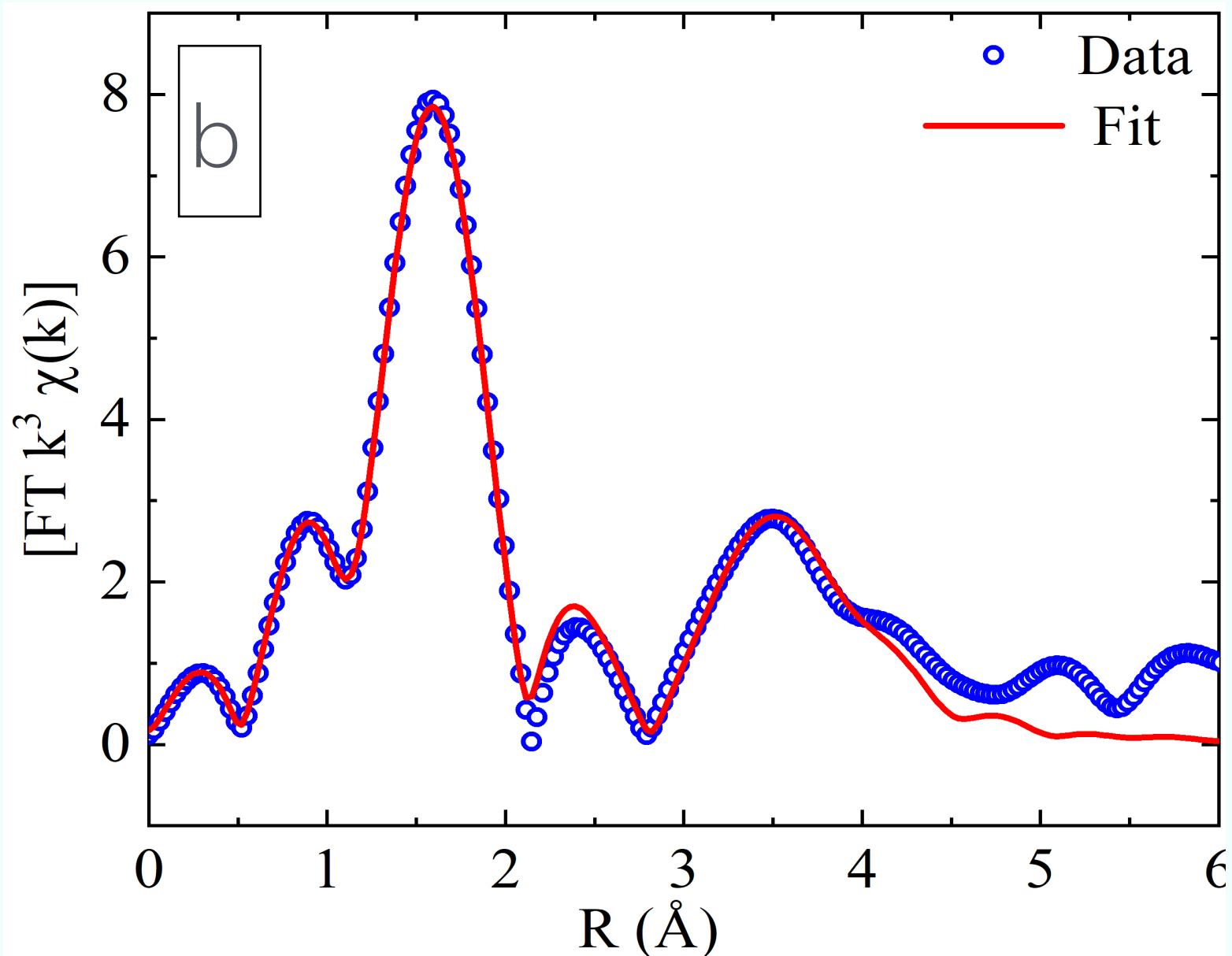
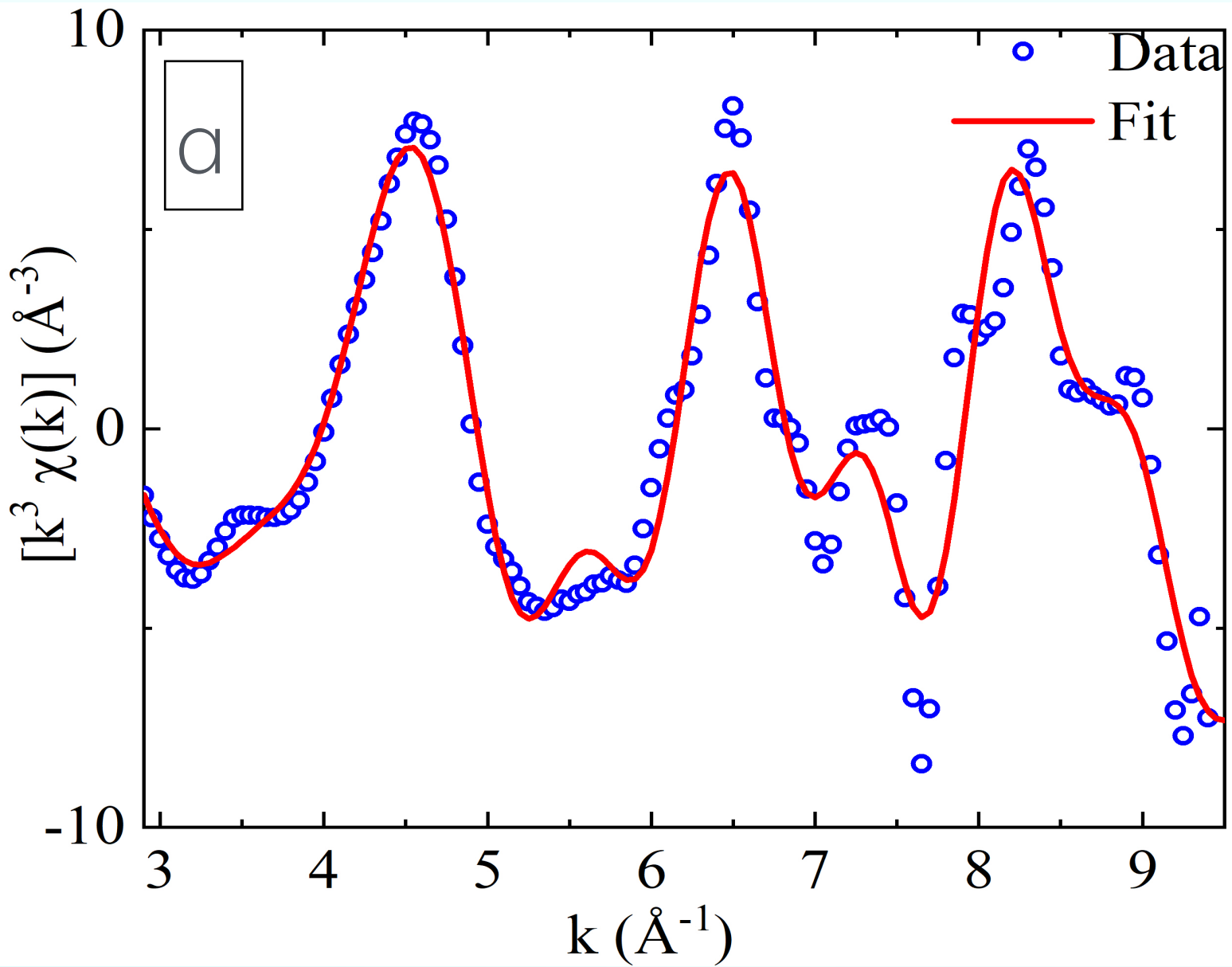


At Ba L_3 -edge

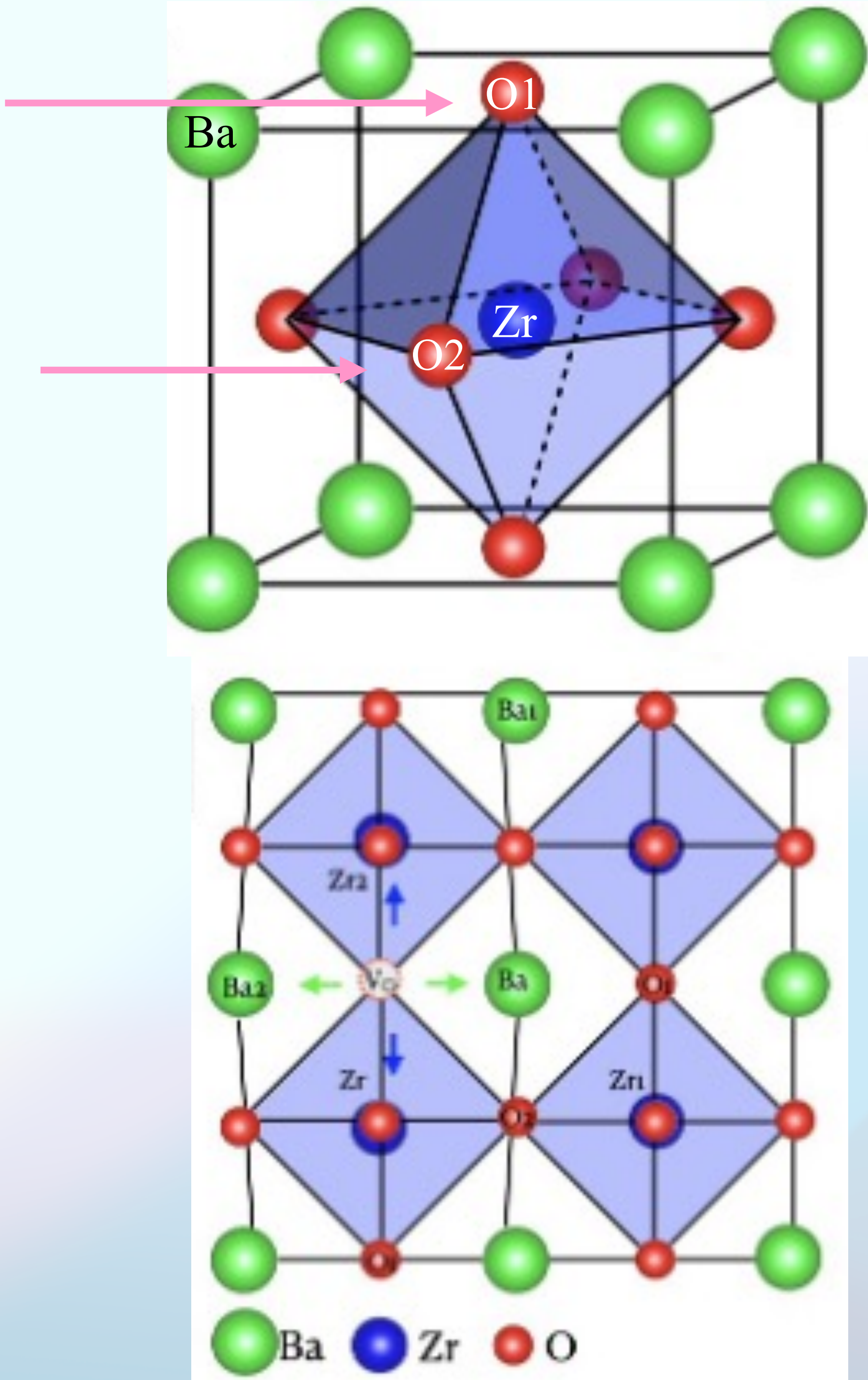
Bond	CN	R ($\text{\AA}$)	σ^2 ($\text{\AA}^2$)	R-factor
Ba-O1	12	2.97 ± 0.006	0.025 ± 0.001	0.019
Ba-Zr1	8	3.65 ± 0.013	0.013 ± 0.001	-
Ba-Ba1	6	3.76 ± 0.017	0.016 ± 0.002	-

In-plane and Out-plane oxygen environment

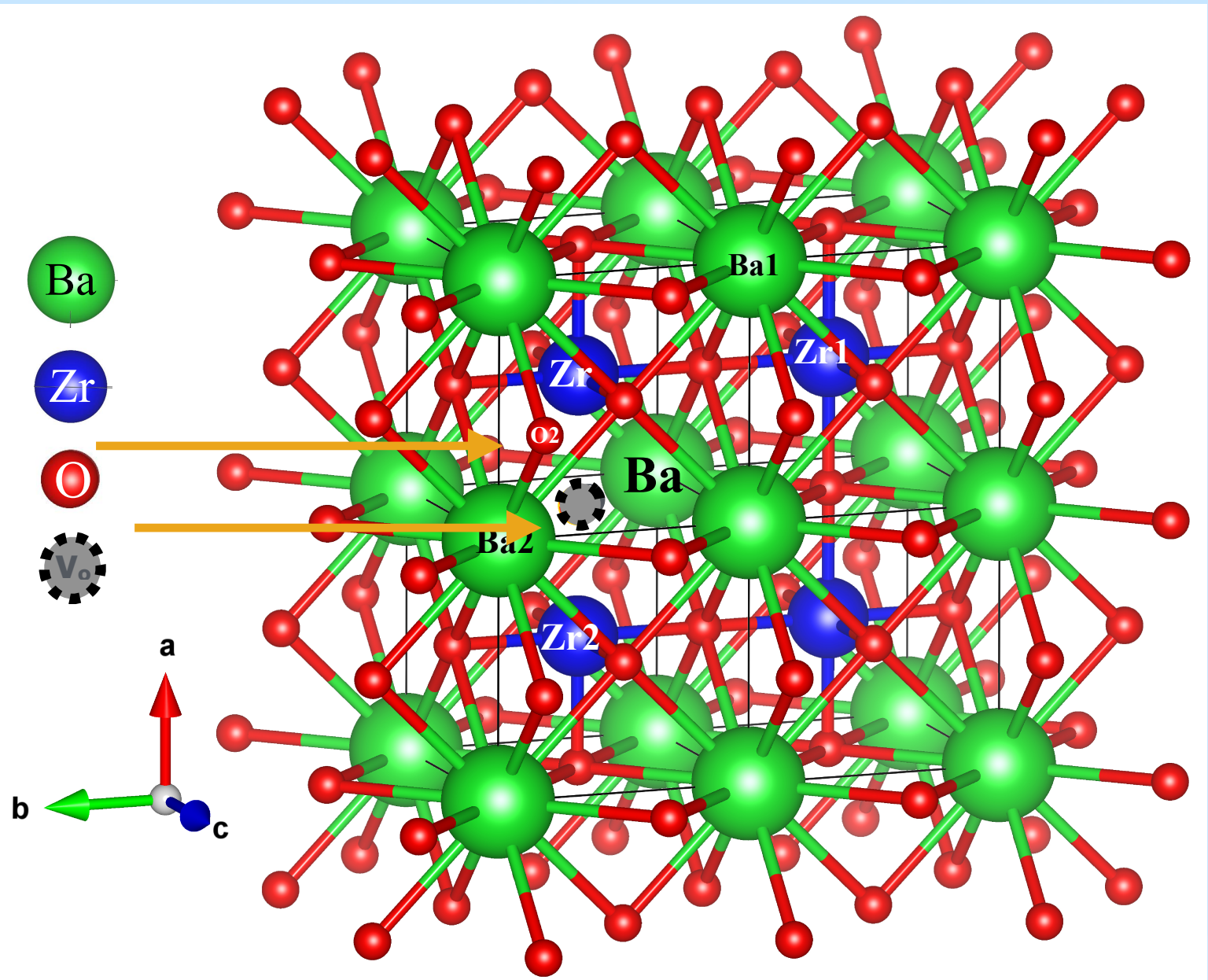
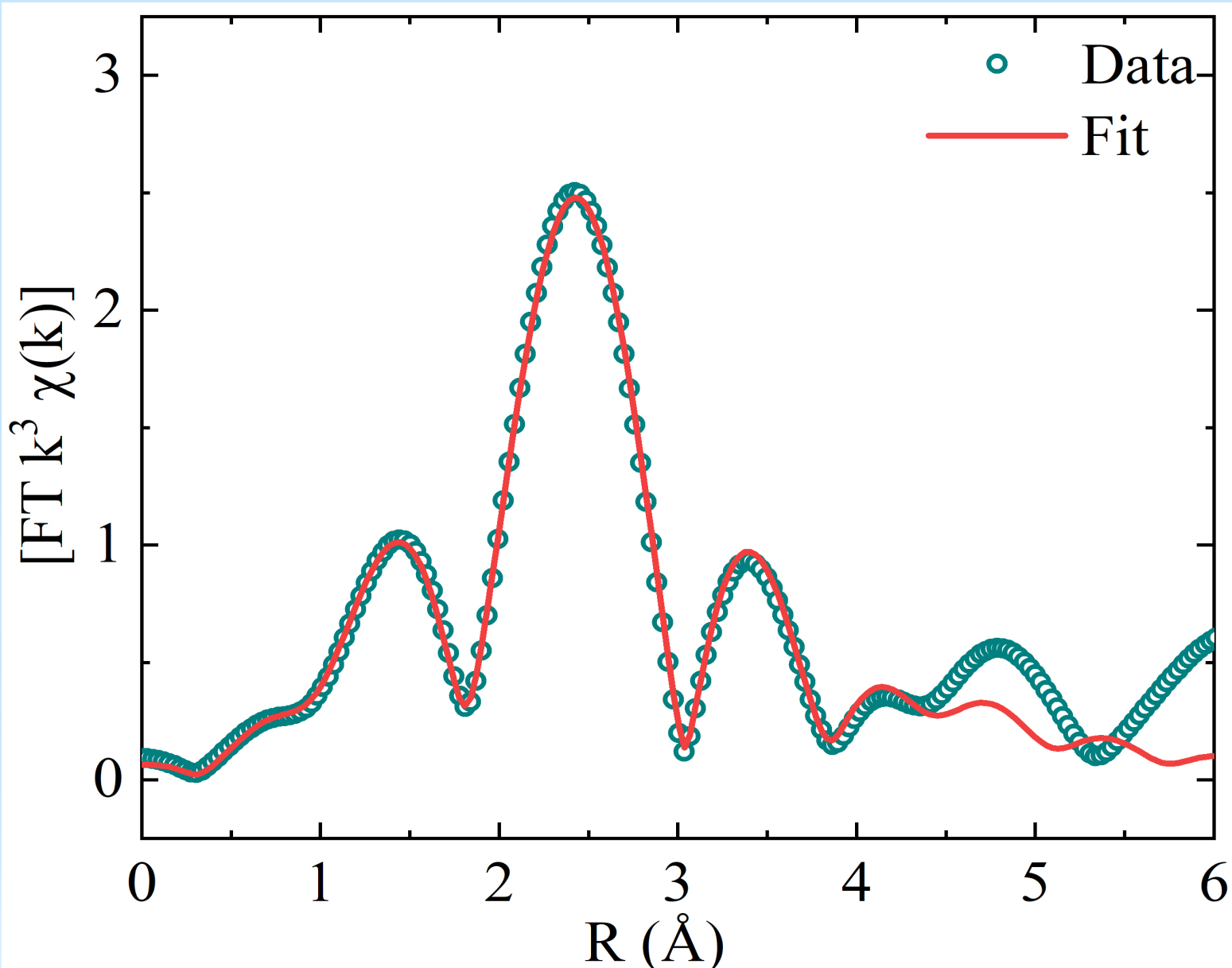
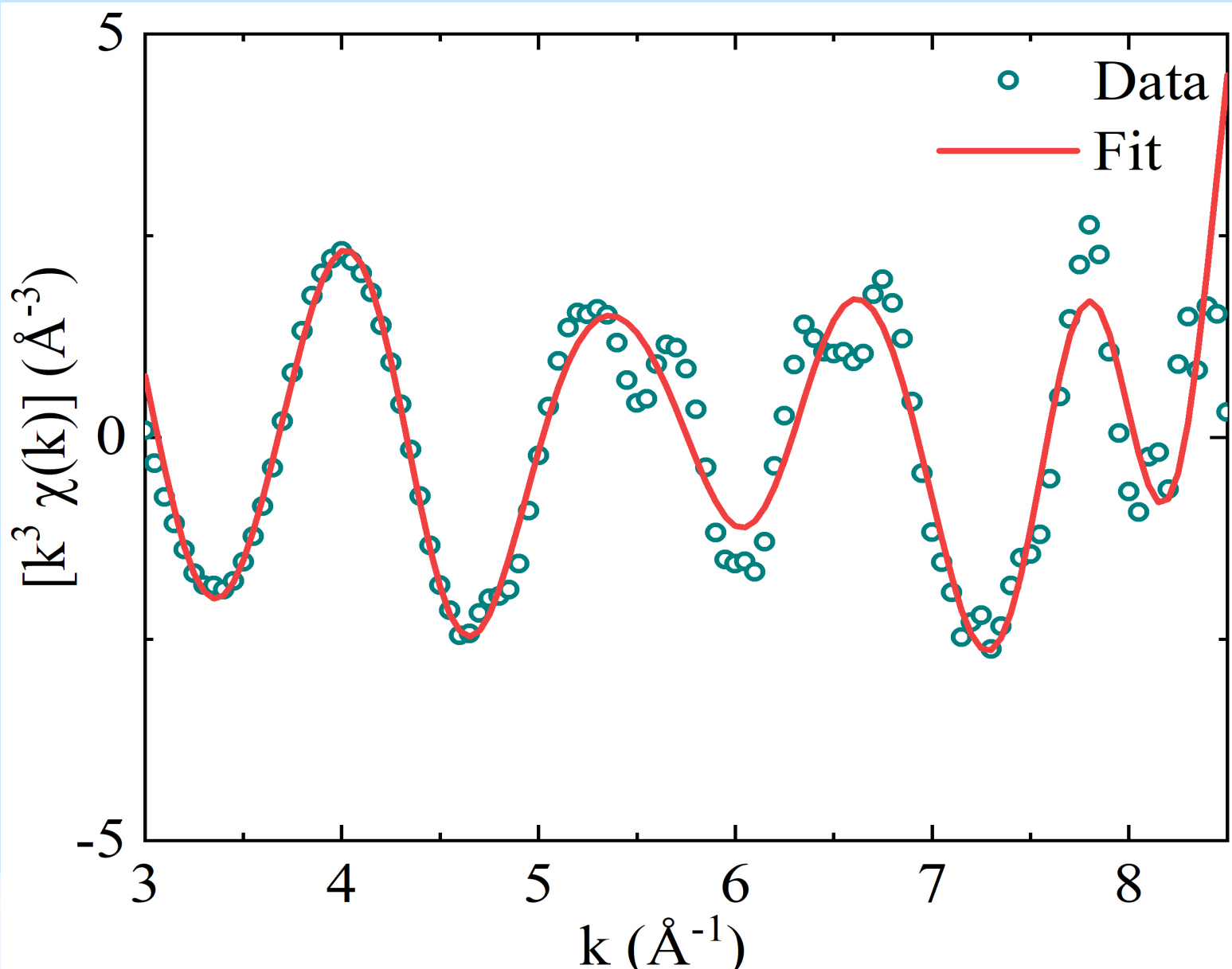
Zr K-edge



Bond	CN	R (Å)	σ^2 (Å)	R-factor
Zr-O2	4	2.13 ± 0.022	0.005 ± 0.0008	0.014
Zr-O1	2	2.01 ± 0.050	0.008 ± 0.002	-
Zr-Ba1	8	3.73 ± 0.017	0.010 ± 0.003	-
Zr-Zr1	4	4.33 ± 0.040	0.006 ± 0.0006	-
Zr-Zr2	2	4.05 ± 0.125	0.007 ± 0.0002	-

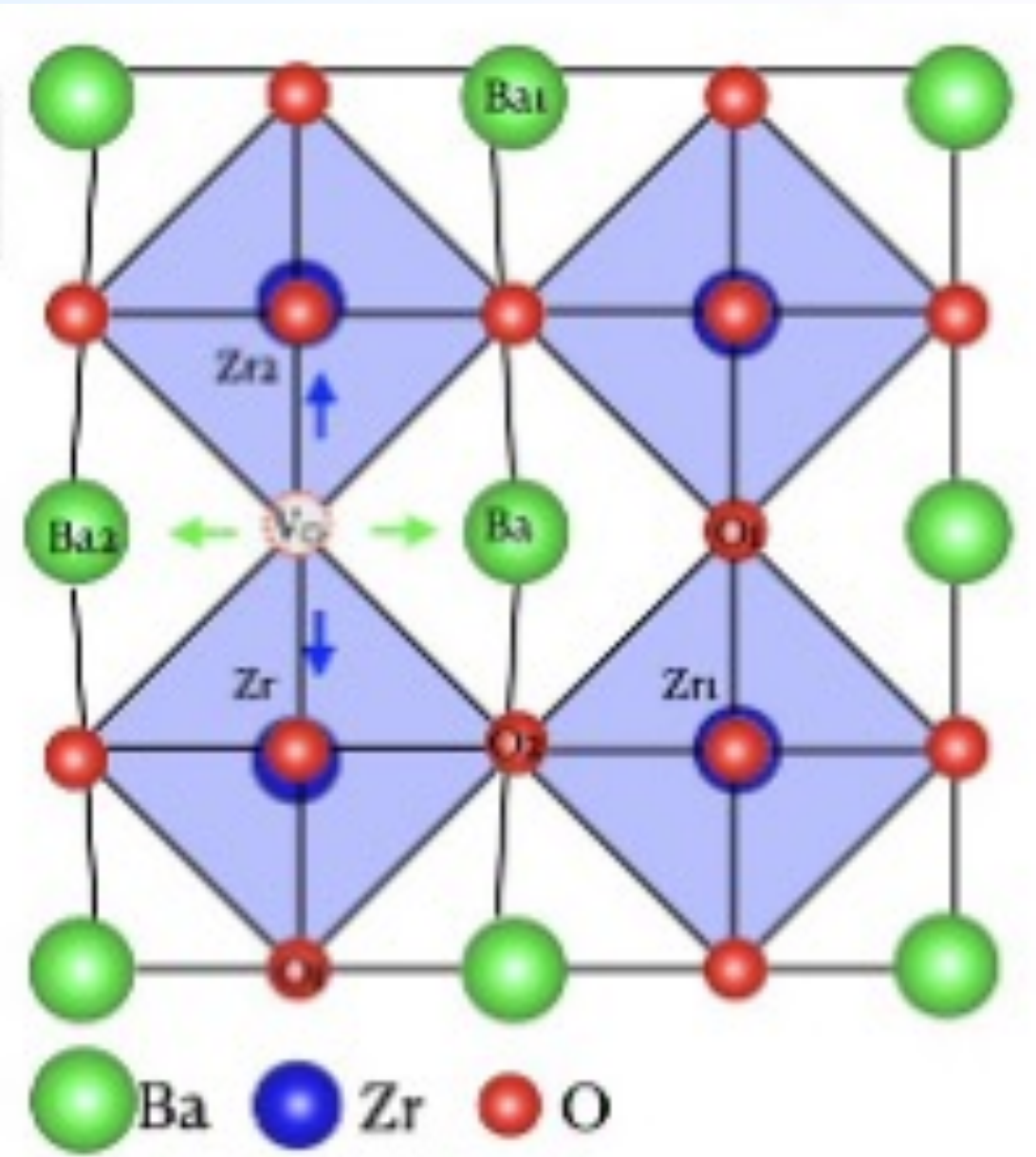


Ba L₃-edge



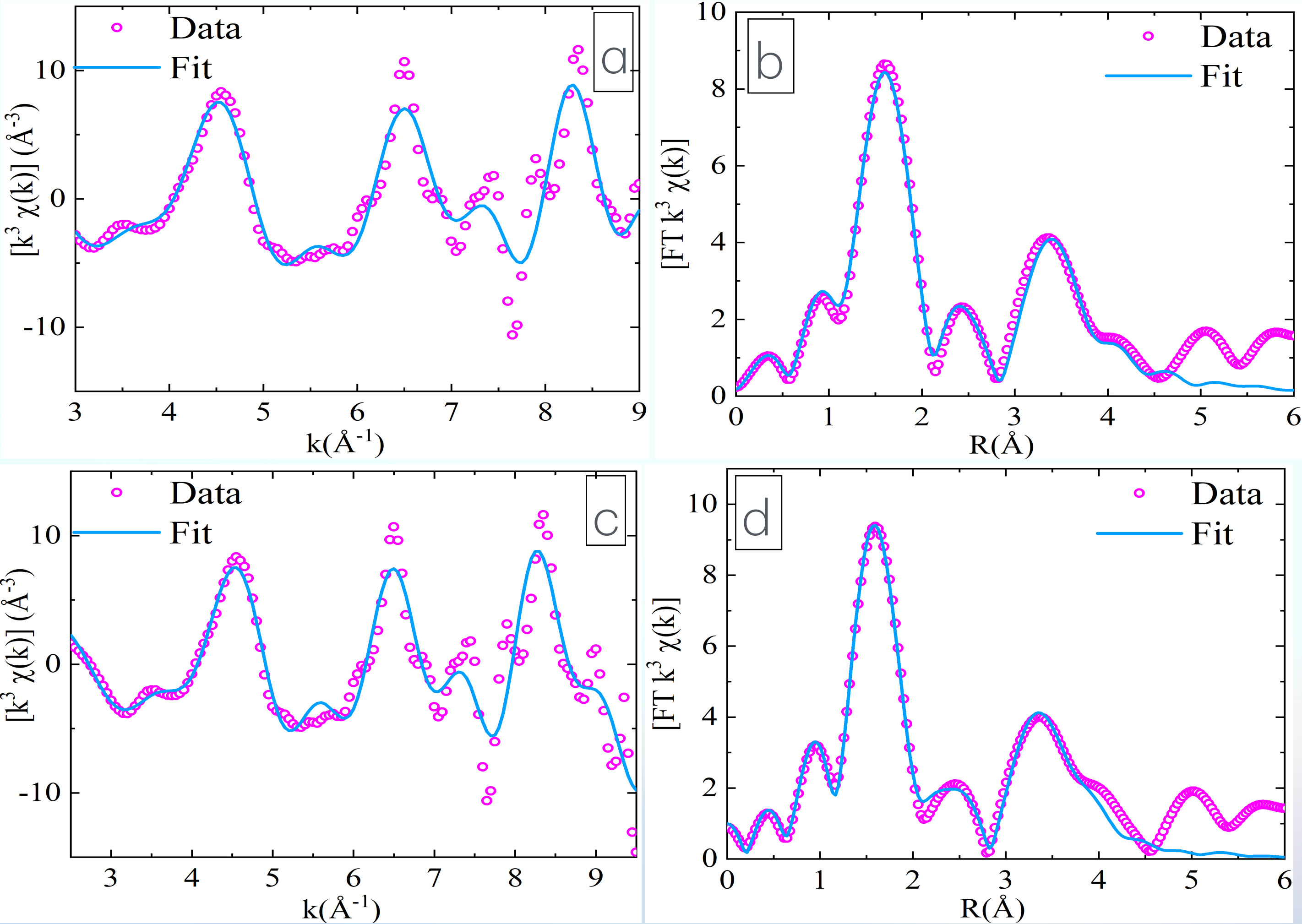
Schematic presentation of in-plane and out-plane oxygen environment at Ba site

Bond	CN	R (Å)	σ^2 (Å)	R-factor
Ba-O1	4	2.66 ± 0.049	0.019 ± 0.011	0.013
Ba-O2	8	2.89 ± 0.018	0.011 ± 0.004	-
Ba-Zr1	8	3.22 ± 0.053	0.029 ± 0.008	-
Ba-Ba1	2	4.19 ± 0.055	0.0009 ± 0.008	-
Ba-Ba2	4	3.94 ± 0.045	0.008 ± 0.006	-



Temp-dependent EXAFS study at Zr K-edge

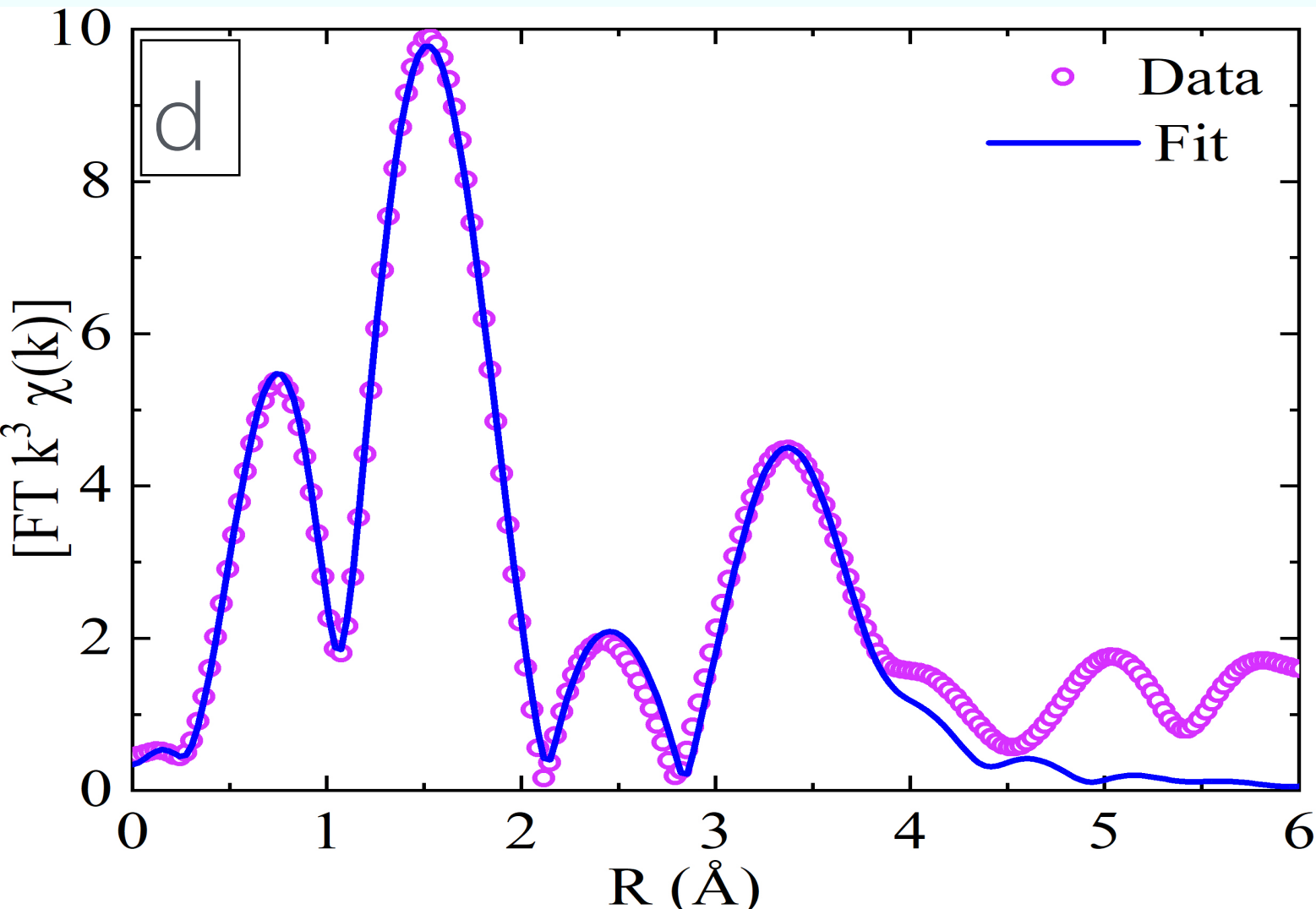
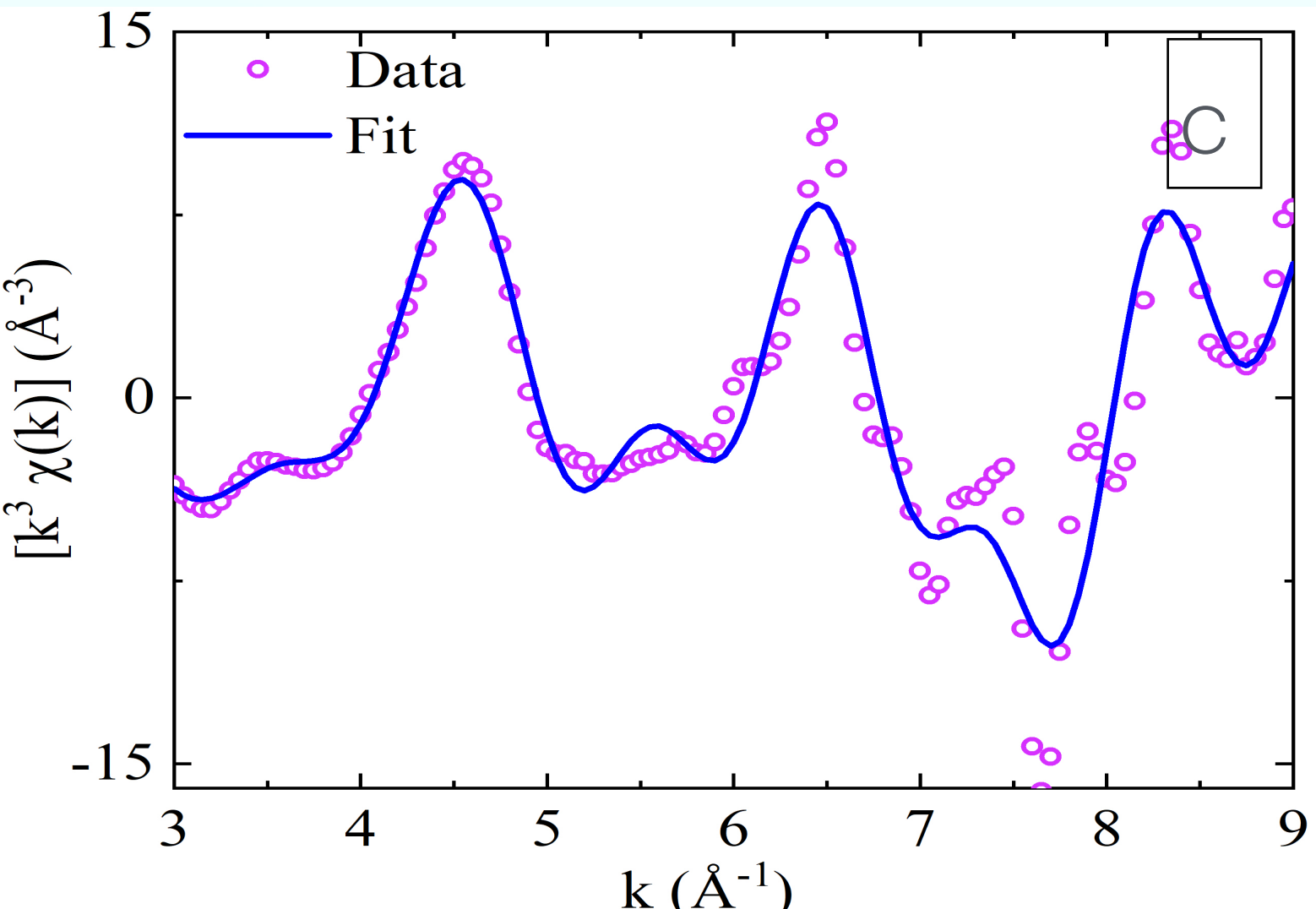
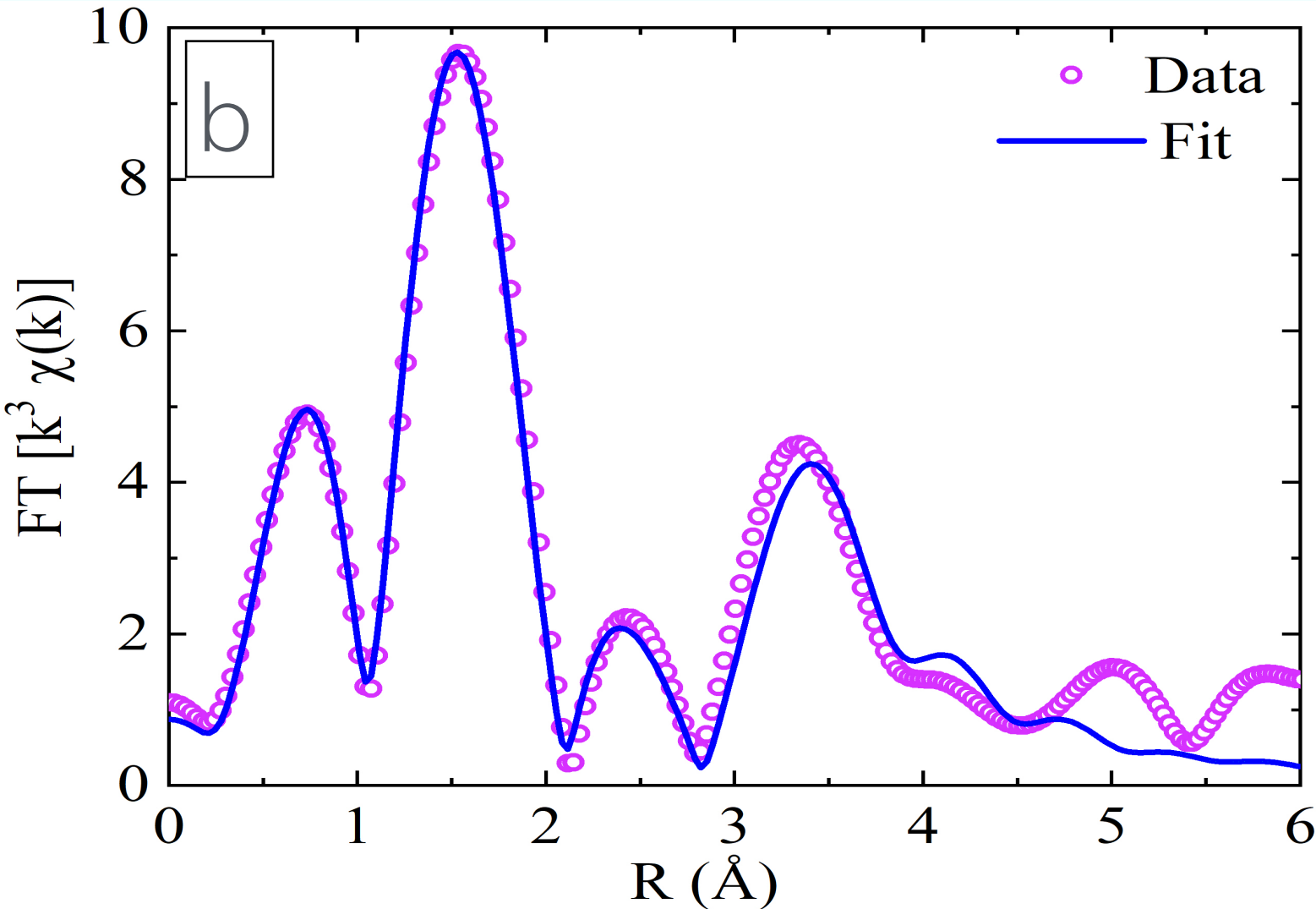
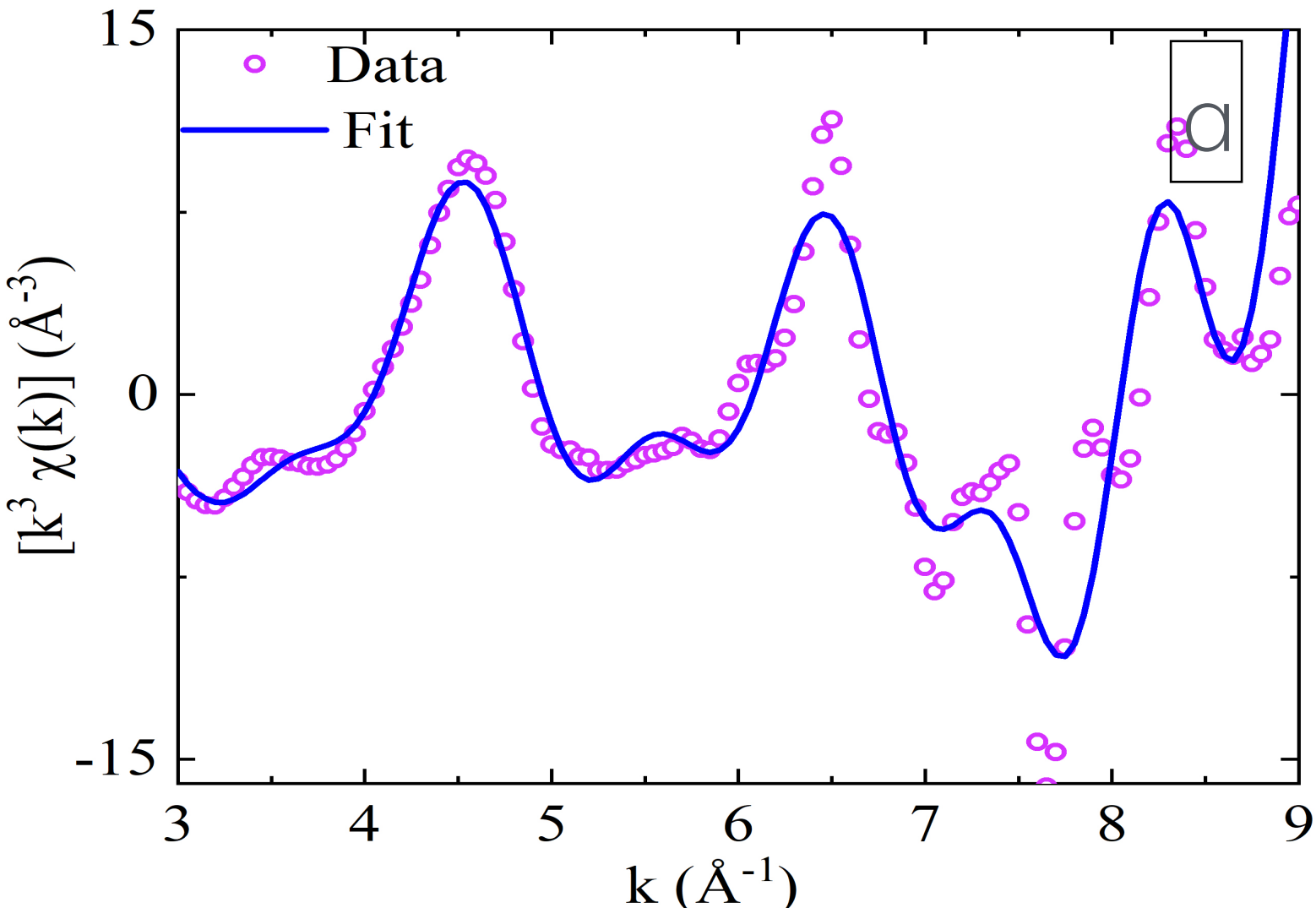
100 K



Bond	CN	R (Å)	σ^2 (Å)	R-factor
Zr-O1	6	2.11 ± 0.005	0.004 ± 0.0009	0.026
Zr-Ba1	8	3.74 ± 0.010	0.006 ± 0.001	-
Zr-Zr1	6	4.13 ± 0.108	0.021 ± 0.018	-

Bond	CN	R (Å)	σ^2 (Å)	R-factor
Zr-O2	4	2.10 ± 0.012	0.0002 ± 0.0017	0.018
Zr-O1	2	1.96 ± 0.029	0.009 ± 0.008	-
Zr-Ba1	8	3.68 ± 0.015	0.008 ± 0.003	-
Zr-Zr1	4	4.26 ± 0.072	0.003 ± 0.008	-
Zr-Zr2	2	3.97 ± 0.058	0.007 ± 0.008	-

82K

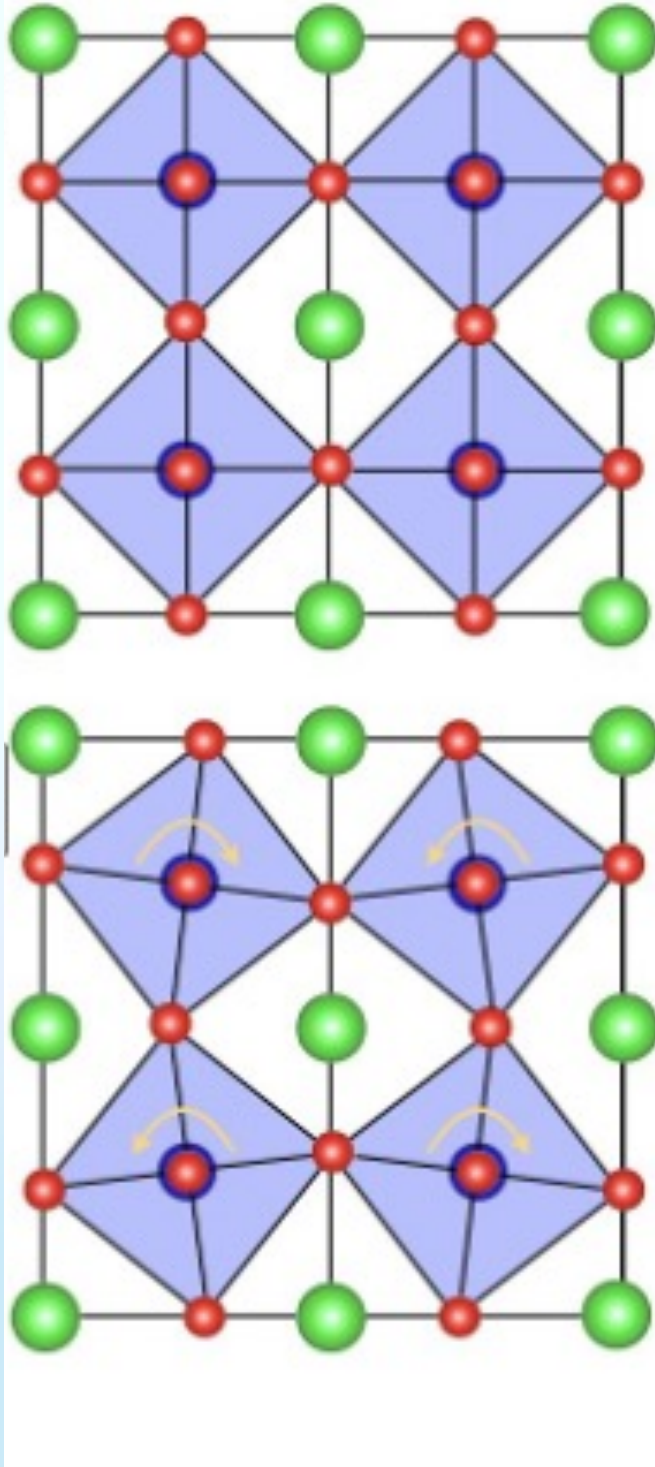


We do not see tetragonal signal at 82K!

Bond	CN	R (Å)	σ^2 (Å)	R-factor
Zr-O1	6	2.12 ± 0.006	0.003 ± 0.001	0.019
Zr-Ba1	8	3.77 ± 0.016	0.003 ± 0.002	-
Zr-Zr1	6	4.18 ± 0.065	0.010 ± 0.009	-

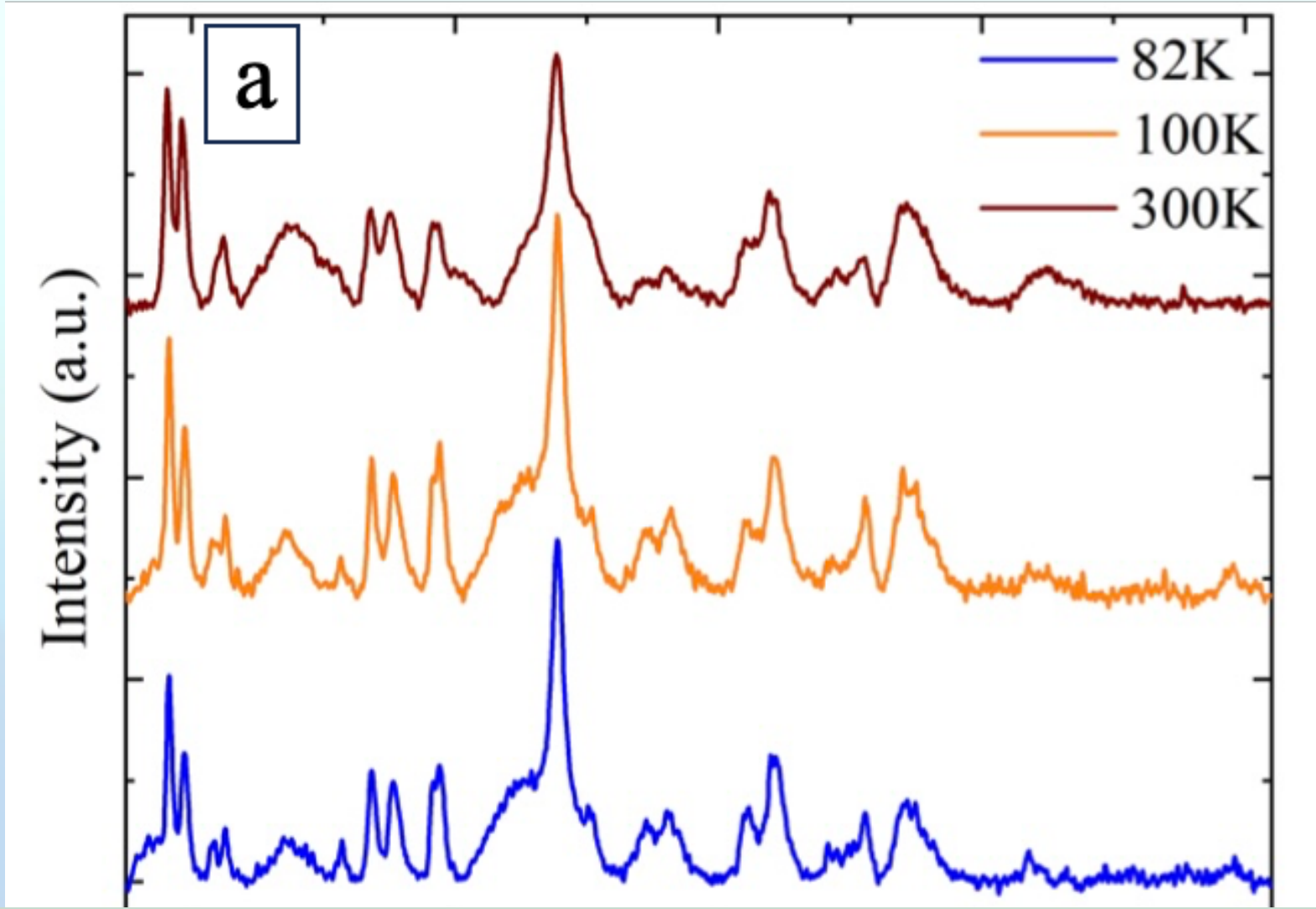
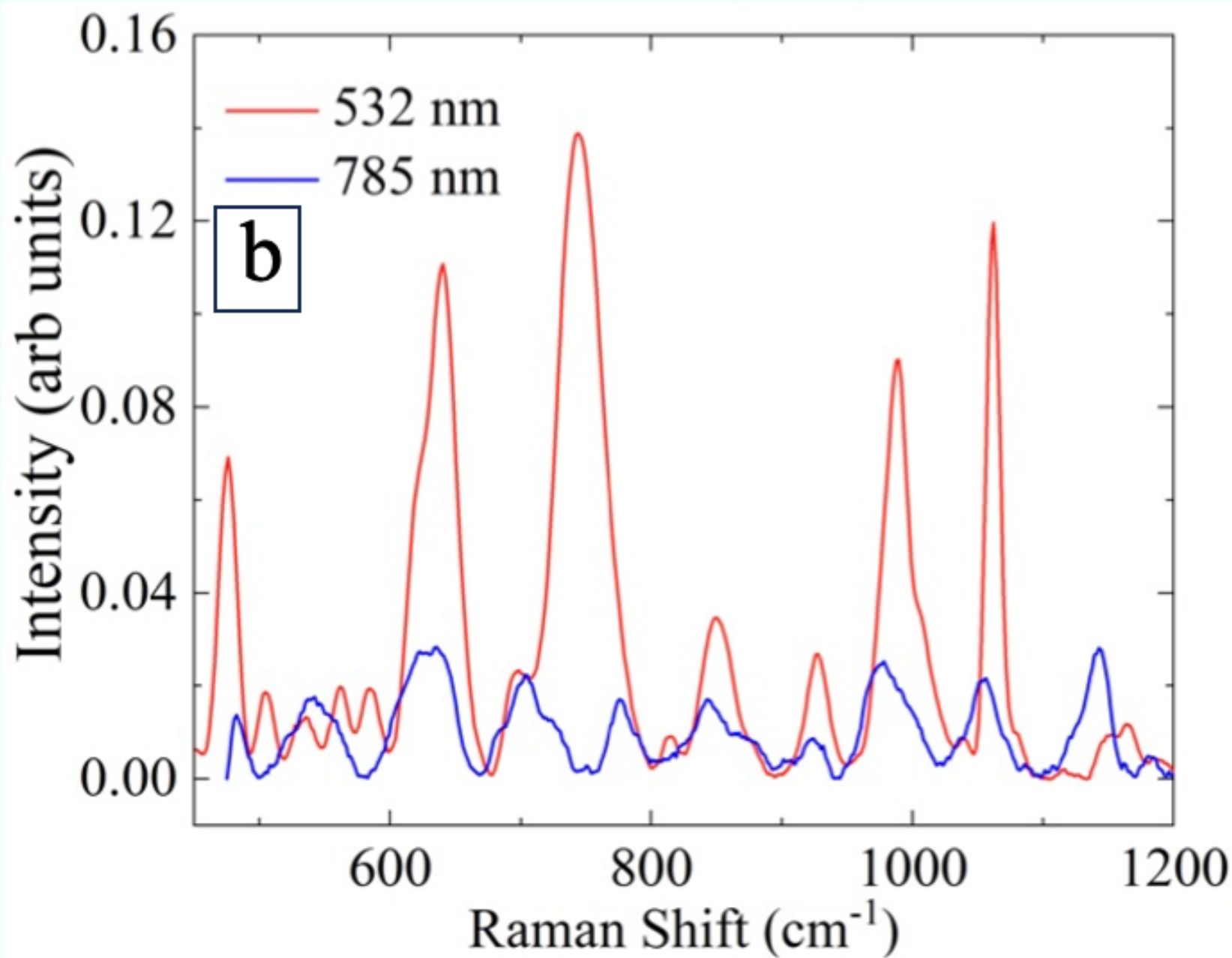
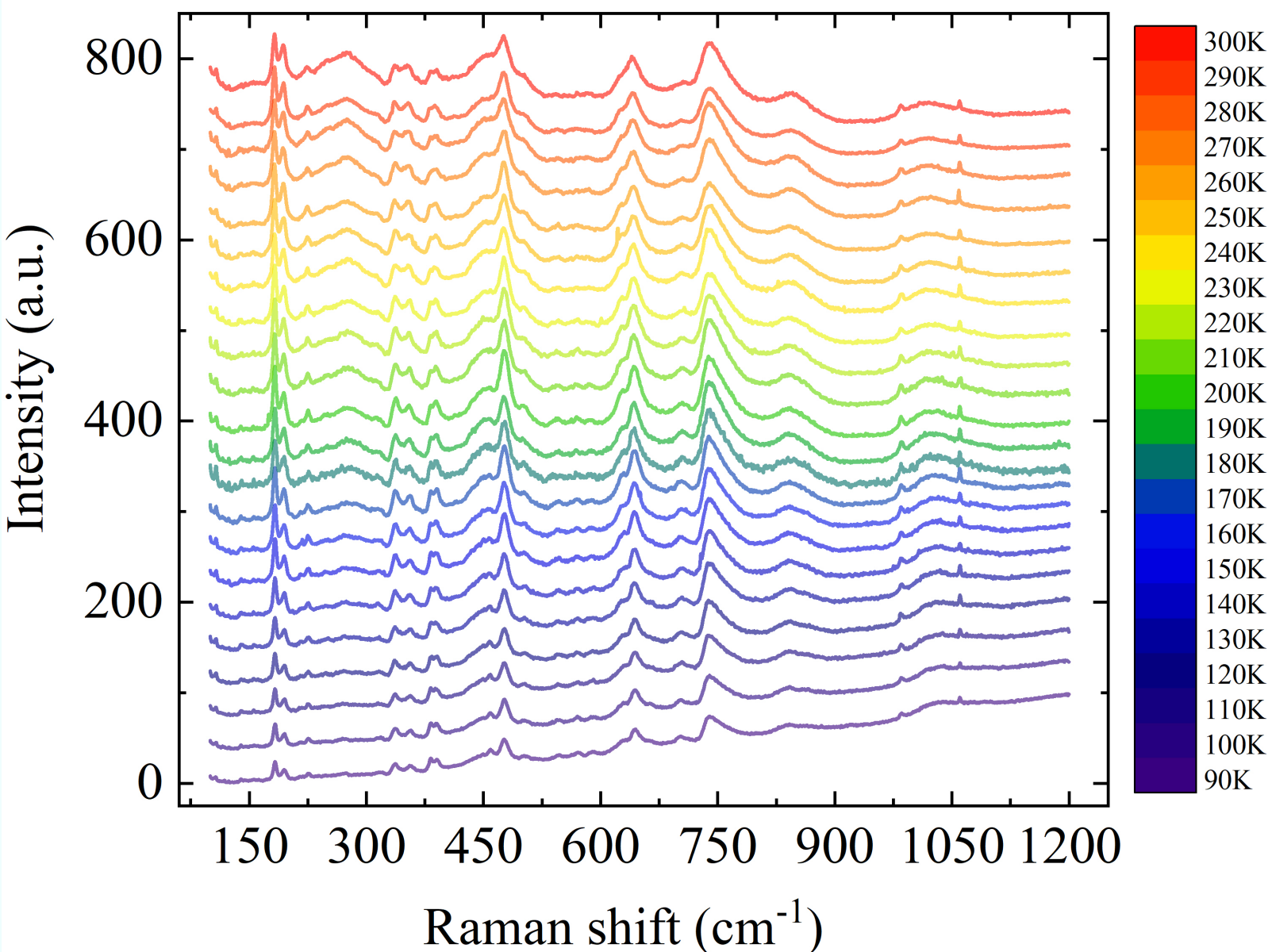
Schematic of ZrO₆ octahedral rotation at transition temperature

82 K is transition temperature, ZrO₆ octahedral rotation also participated



Bond	CN	R (Å)	σ^2 (Å)	R-factor
Zr-O2	4	2.10 ± 0.017	0.0009 ± 0.0002	0.016
Zr-O1	2	1.89 ± 0.047	0.015 ± 0.012	-
Zr-Ba1	8	3.68 ± 0.025	0.011 ± 0.004	-
Zr-Zr1	4	4.19 ± 0.321	0.024 ± 0.038	-
Zr-Zr2	2	3.93 ± 0.106	0.005 ± 0.008	-

e. Raman Spectroscopy



There are no significant alterations occur at ~80 K, where supposedly tetragonality arises at the nano domains even where dielectric anomalies start to appear, so we believe that these are due to second-order Raman modes enhances by vacancy disorder..

Raman modes obtained with all three laser excitation compared with literature

freq. cm ⁻¹							
473	473	532	785	Theoretical	Combination	Associated Displacement	Atomic
nm(RT)	nm(90 K)	nm(RT)	nm(RT)				
182	183			193	overtone Γ_4^-	Last (TO) zone center mode	Ba
193	194			195	overtone R_5^+	antiparallel displacements	
223	225			262	overtone X_1^+	antiparallel Ba displacements (x)	
253				266	overtone Γ_4^-	Last (LO) zone center mode	
279	269			277	$\Gamma_4^- \oplus \Gamma_5^-$	Last (TO)+shear mode octahedra	
	315			277	$X_5^+ \oplus X_5^+$	antiparallel Ba displacements (x,y) + antiparallel oxygens (x,y)	
				280	overtone M_3^-	antiparallel Zr displacements (z)	
337	337					distortion of the oxygen octahedra [8]	
351	356						
388	382						
451	454	475	483	451	$R_5^+ \oplus R_5^+$	Ba (antiparallel) + octahedra rotations	
476	477						
501	503	504					
	546	531	541				
	570	562					
	589	583					
622	627	627	619				
640	644	642	639	636	$\Gamma_4^- \oplus \Gamma_4^-$	Last (LO) + Axe (TO) zone center modes	
692	701	695	706	707	overtone R_5^+	"scissoring" mode of octahedra	

Charged oxygen (anion) vacancy is responsible for such intense second order Raman signal at room temperature!

4. Overall Conclusions & Future Scope

1. Lab source XRD confirms long range cubic symmetry present in BZO system throughout temperature range 30-300 K, but Synchrotron XRD confirms asymmetry arises near the ~80K temp indication of presence of defect.
2. Stable charged vacancy confirmation by ab-initio thermodynamics calculation and also confirm by UV-Vis and XPS results.
3. UV-Vis shows two band gap values 3.86 eV and 5.04 eV correspond to vacancy formation and band to band transition (VBM to CBm) confirms shallow donor states lies down to conduction band minimum evident by urbach energy analysis.
4. EXAFS analysis shows that oxygen vacancy creates local disordered breaks inherent cubic symmetry and responsible for intense Raman modes in Centrosymmetric -cubic system.
5. Raman spectra collected in the range 300-800 cm⁻¹ and 785 nm, confirm that no phase change occurs in temperature ~80 K
6. **Concluded that anion vacancy breaks inherent cubic symmetry and lifts up Raman modes in the 300-800 cm⁻¹ range.**

PHYSICAL REVIEW B **111**, 104107 (2025)

Oxygen vacancy mediated local symmetry breaking drives intense Raman modes in BaZrO₃

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5. Acknowledgements



विज्ञान एवं प्रौद्योगिकी विभाग
DEPARTMENT OF
SCIENCE & TECHNOLOGY



ज्ञान-विज्ञान विमुक्तये

University Grants Commission



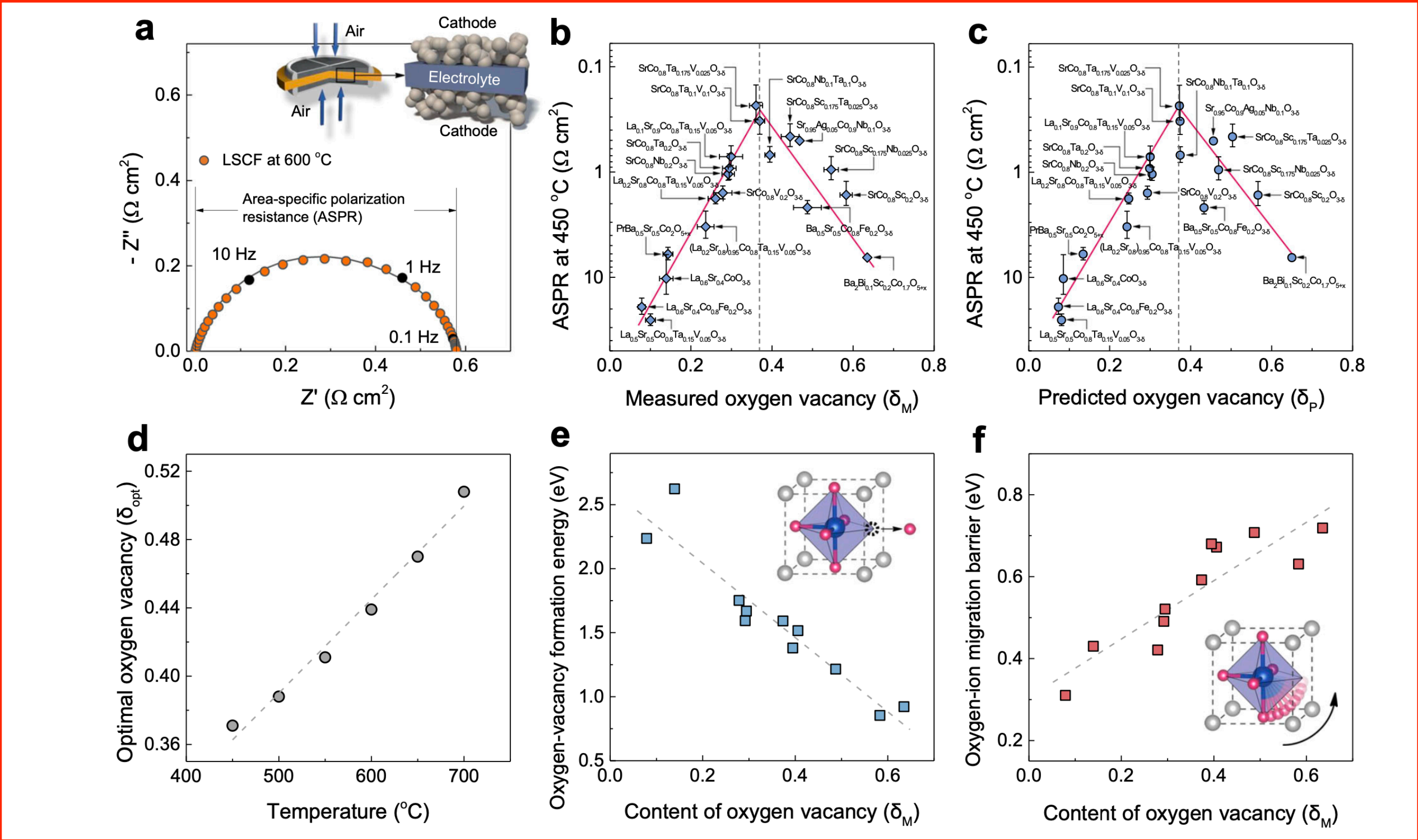
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Future Scope

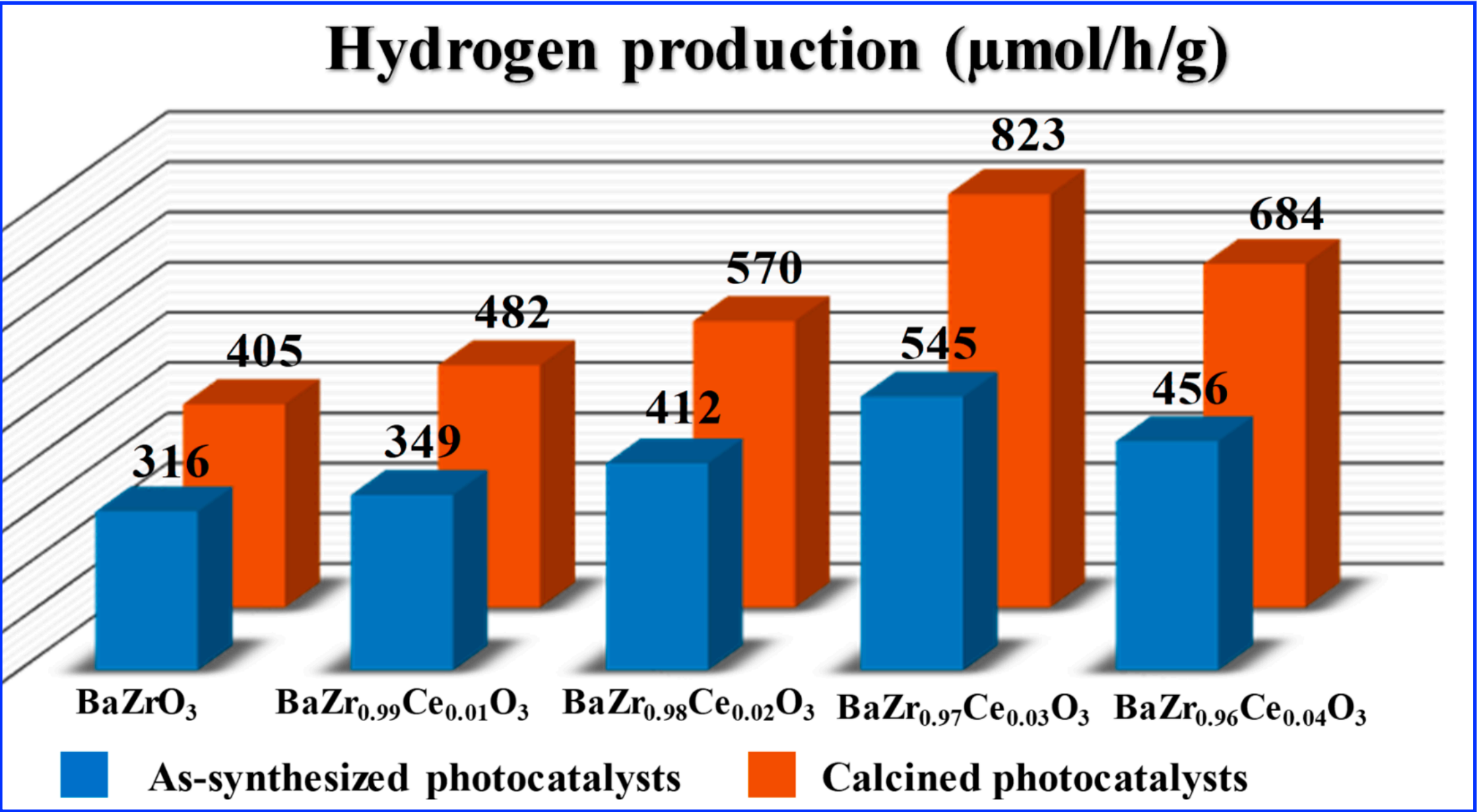


Zhiheng Li, *et.al*, Nature Comm. 15, 9318 (2024)

1. Optimizing vacancy concentration in pristine and doped BZO for improved electrocatalytic /photo-electrocatalytic activity.
2. Strain engineering in BZO Thin films.
3. EXAFS study at low temperature (down to 10K) at Ba LIII-edge, Zr K-edge to gain insights of the nano-domain phase transition.

Tuning oxygen vacancy can enhance the electrocatalytic activity in cubic perovskites.

By modulating dopants and oxygen vacancy in BZO, one can enhance their photo-electrocatalytic activity.



Anindya S. Patra, *et.al*, J.Phys.Chem.C 123, 233 (2019)

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8. Thanks to all my batchmates Meenal, Isha, Shivam, Samanway, Nitin for cheering me up and my junior Smritiparna, Koushik, Nayan and my senior for helping me out
9. Special thanks to My guide Dr. Debalaya Ma'am for believing in me and pushing me hard in this journey and Dr. Deshpande sir for their encouragement

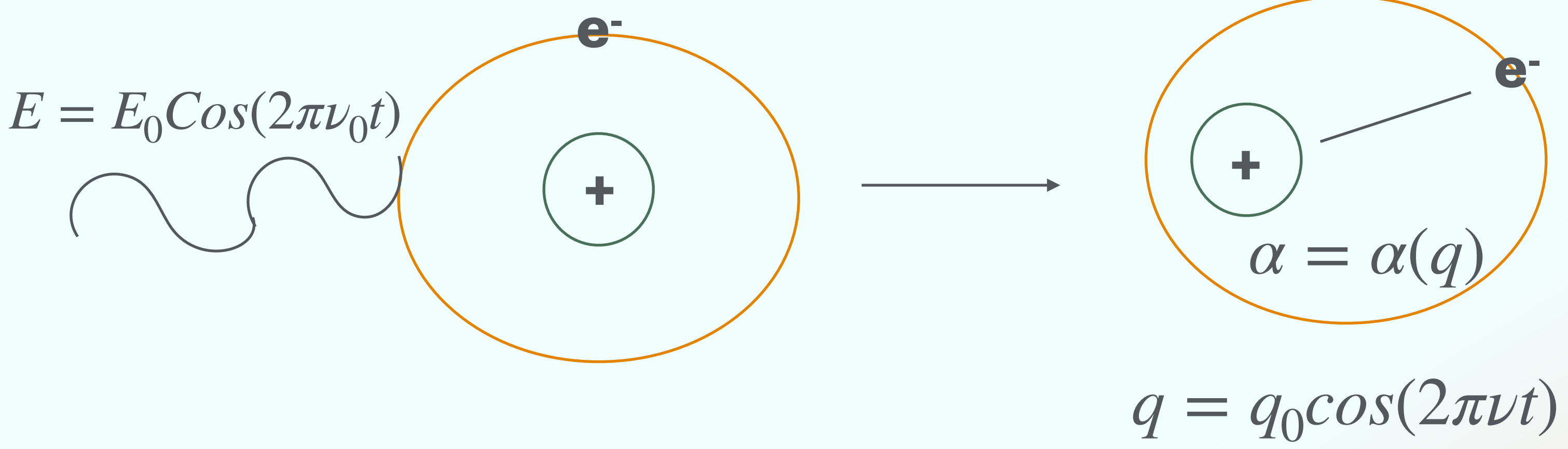
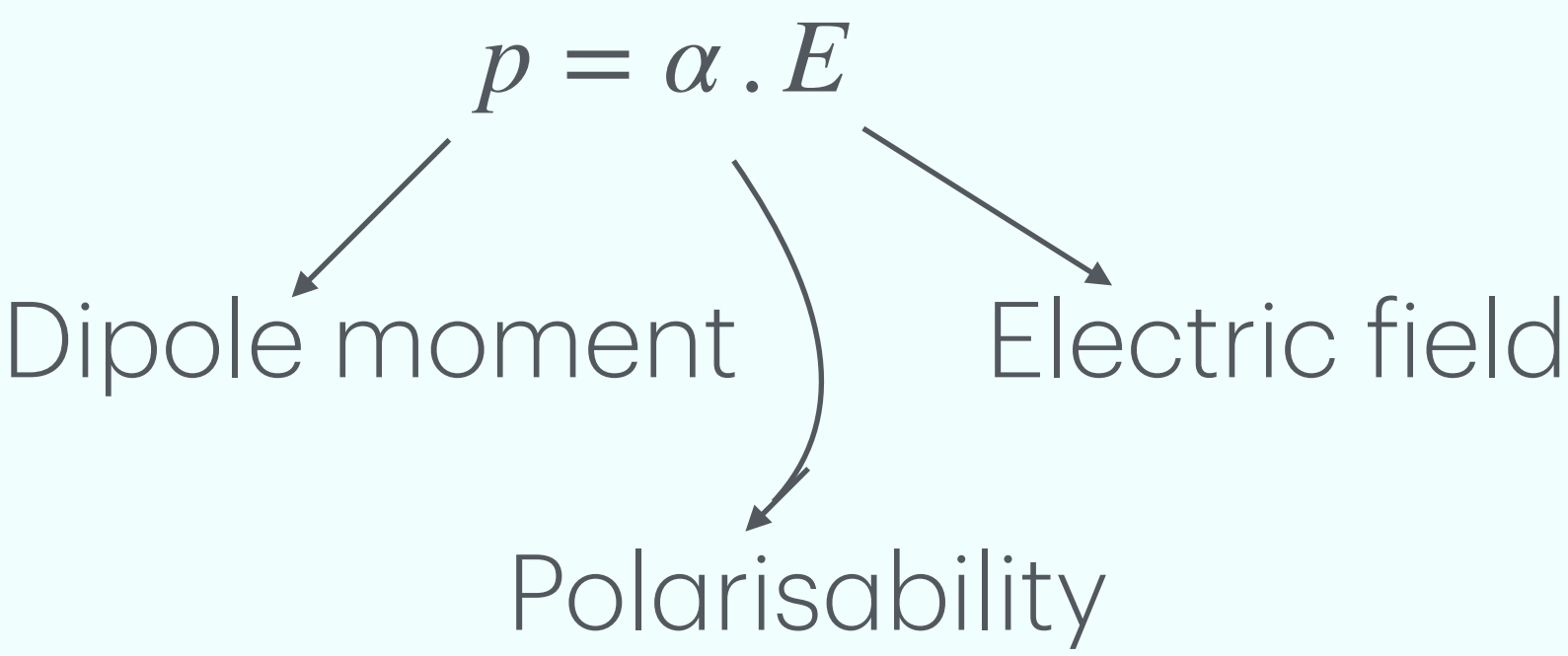
Conferences

1. Presented Poster in International Conference IUMRS-ICA 2022 at IIT-Jodhpur
2. Attended International Conference ICOPVS at UGC-DAE CSR Indore
3. Presented Poster in International Conference ICAM-GOA 2023 at University of GOA
4. Presented poster in International Conference IUMRS-ICA 2024 at UGC-DAE CSR, Indore
5. Presented Poster in 68th DAE-SSPS 2024 at BARC, Mumbai
6. Presented Poster in IOP Golden- Jubilee Young Women Scientist Meet (IGJYWSM-2024) at IOP-Bhubneshwar

Workshops

1. Attended 2 days hands-on session on Electrochemistry at PDEU, Gandhinagar
2. Attended workshop and Hands-on training on Electrochemical techniques 2024 held at CSIR-AMPRI Bhopal

Theory of Raman Scattering



$$p = \alpha_0 E_0 \cos(2\pi\nu_0 t) + \underbrace{q/2 [\delta\alpha/\delta q]_0 [\cos 2\pi(\nu_0 + \nu_m)t + \cos 2\pi(\nu_0 - \nu_m)t]}_{\text{Inelastic scattering}}$$

Elastic scattering

Inelastic scattering

Raman scattering

$$\delta\alpha/\delta q \neq 0$$

Necessary condition

Antistock lines

Stock lines

First-Order Raman Scattering

Rayleigh Scattering

Key-points

Aspect	First Order Raman	Second-order Raman
Phonon involved	Single phonon	Two phonons (combinations)
Symmetry	Requires polarisability change	Activated by symmetry breaking or defects
Resonance effects	Weak or absent	Strong under excitonic resonance

$$p = \alpha_0 E_0 \cos(2\pi\nu_0 t) + \frac{q}{2} [\delta\alpha/\delta q]_0 [\cos 2\pi(\nu_0 + \nu_m)t + \cos 2\pi(\nu_0 - \nu_m)t]$$

Elastic scattering

Inelastic scattering

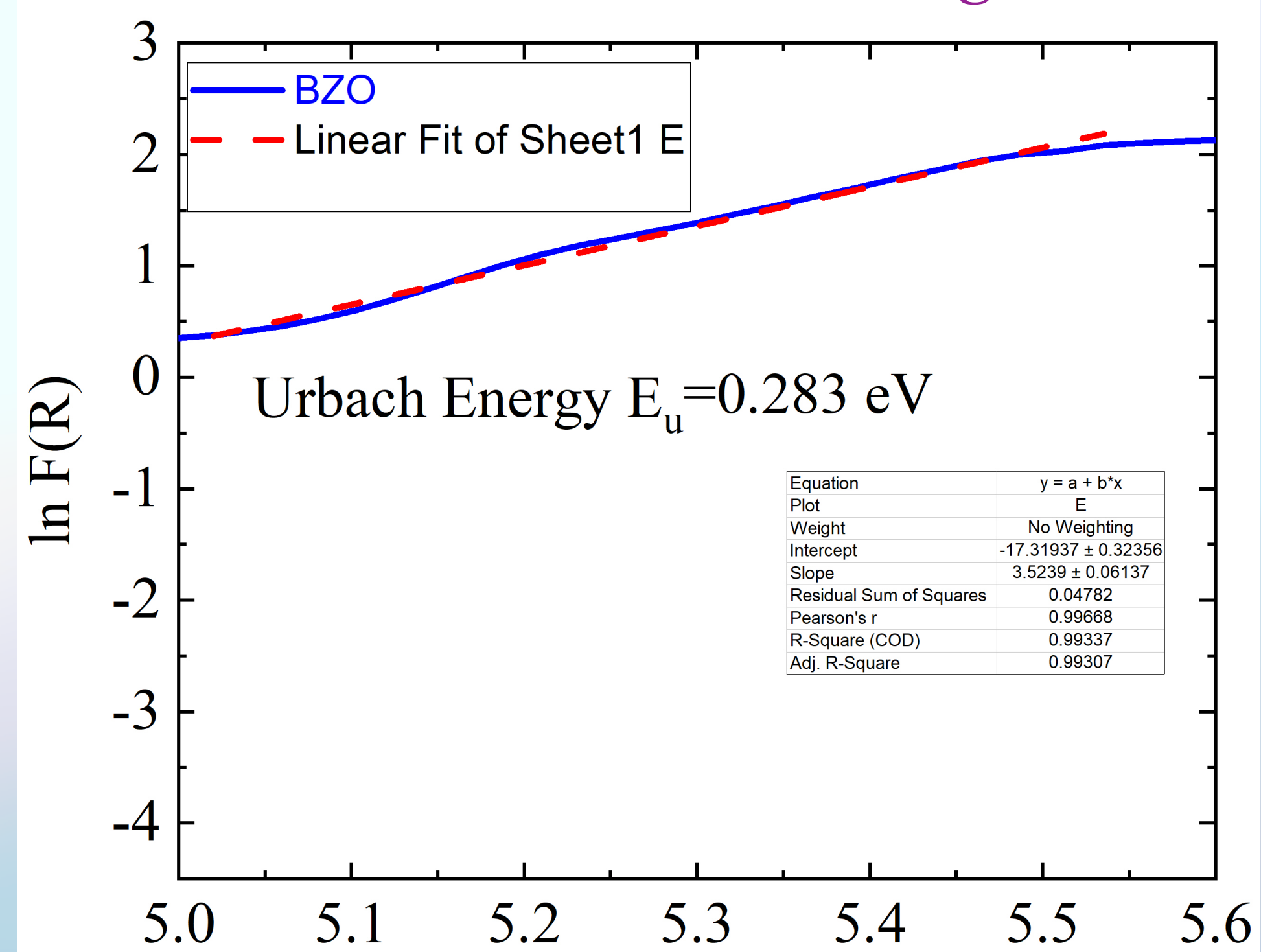
Rayleigh Scattering

Raman scattering $\rightarrow \delta\alpha/\delta q \neq 0$ $\rightarrow$ **First-Order Raman Scattering**
 Necessary condition

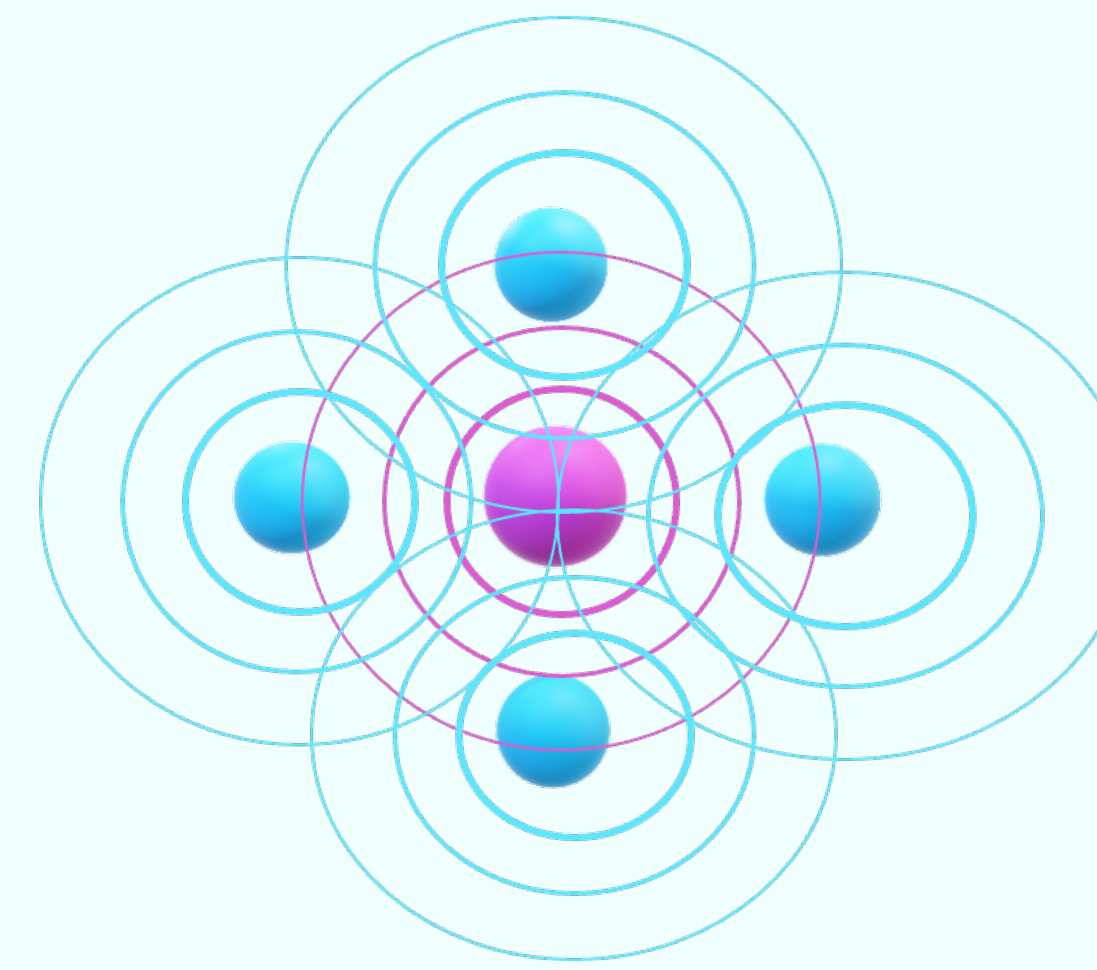
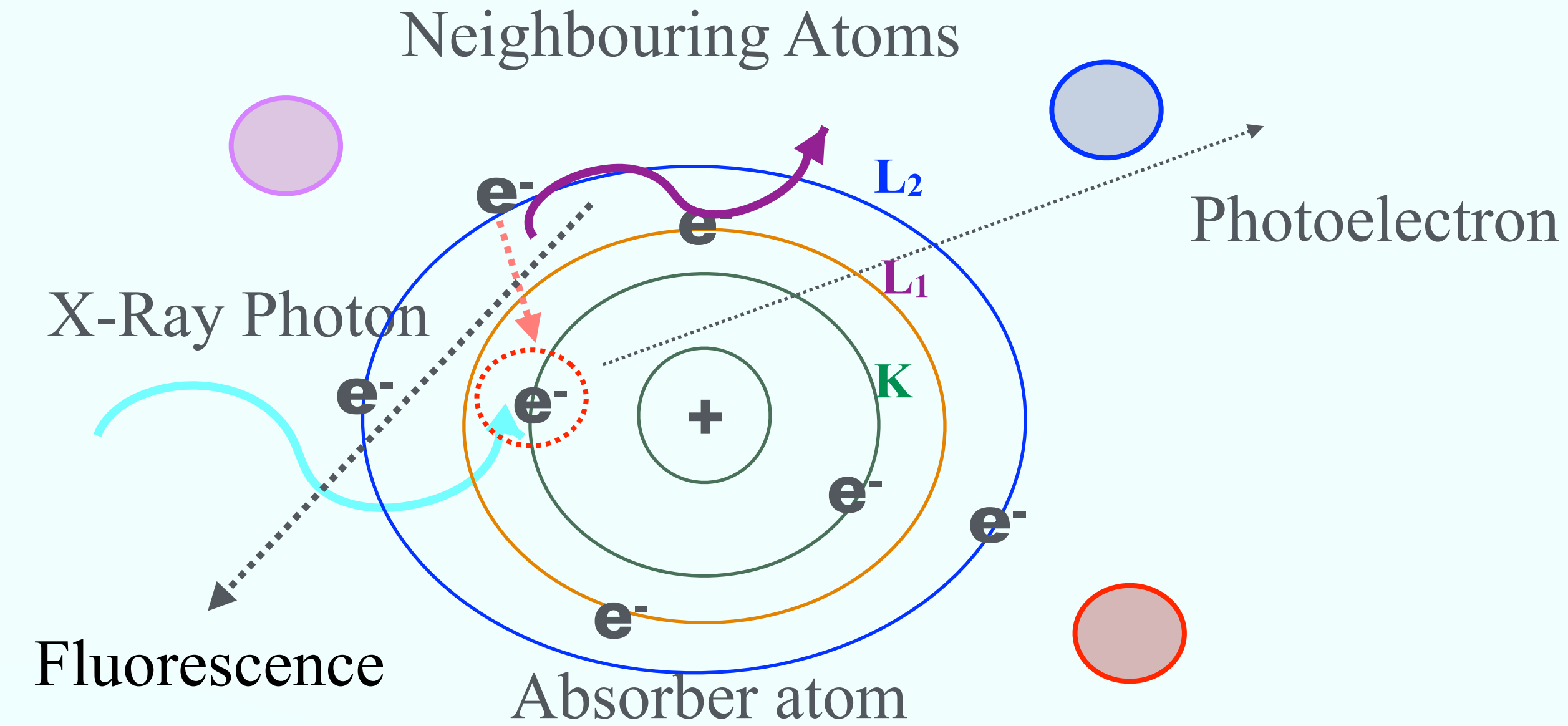
If $\delta\alpha/\delta q = 0$

Higher order term $\delta^2\alpha/\delta q^2$ participated

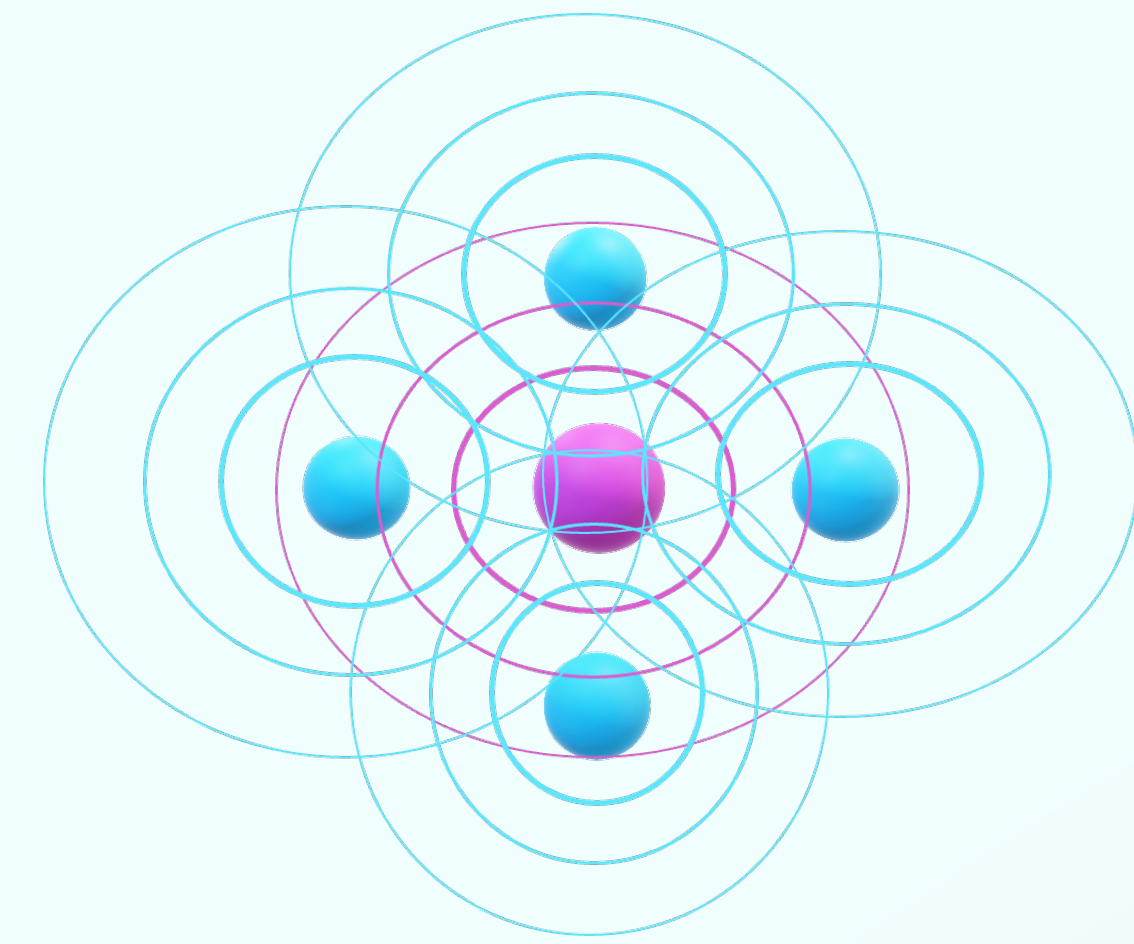
Second-Order Raman Scattering



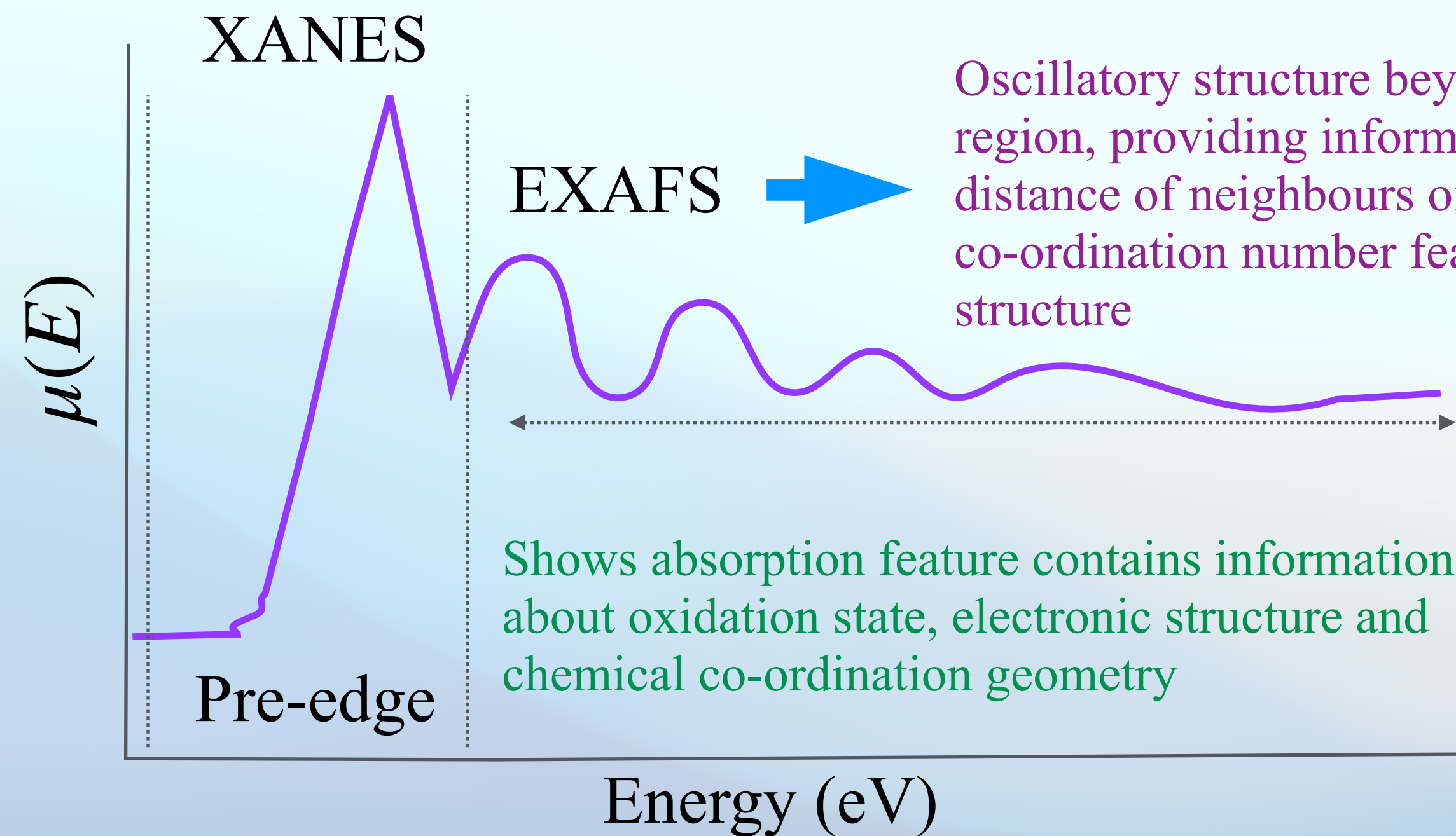
Understanding of EXAFS



Constructive interference



Distructive interference



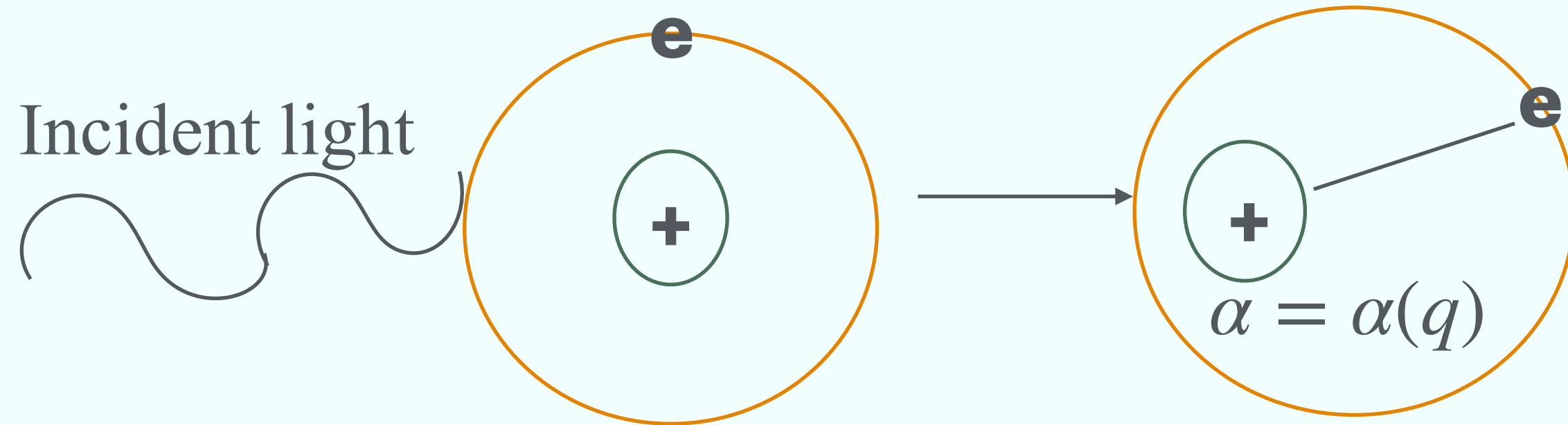
EXAFS Equation

$$\chi(k) = \frac{\sum_j [N_j S_0^2 f(k, \theta) e^{-2k^2 \sigma_j^2} e^{-2R_j \lambda_e(k)}] \sin[2kR_j + \phi(k)]}{kR_j^2}$$

N_j =Co-ordination number, S_0^2 =Amplitude reduction term, $f(\theta, k)$ =Atomic scattering amplitude for single atom scattering, $e^{-2k^2 \sigma_j^2}$, $e^{-2R_j / \lambda_e(k)}$ =amplitude damping term due to thermal motion and electron mean free path, $\phi(k)$ =phase function contribution from the absorber and backscattered electron

Insight of Second-order Raman Scattering

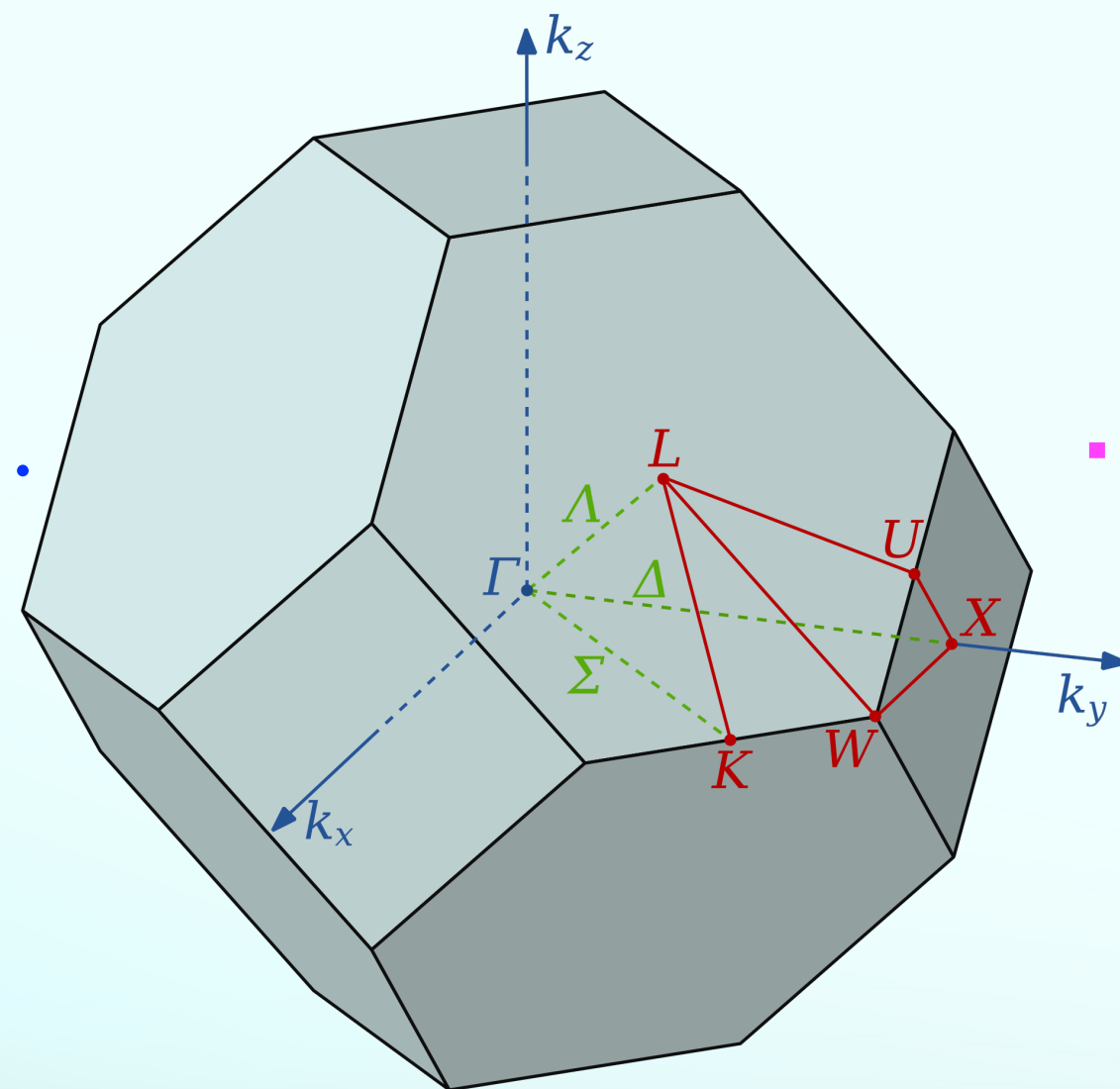
$$\chi_{\alpha\gamma} = (\chi_0)_{\alpha\gamma} + \sum_{i\epsilon} (R_i^\epsilon)_{\alpha\gamma} q_i^\epsilon + \frac{1}{2} \sum_{ij\epsilon n} (R_{ij\epsilon n})_{\alpha\gamma} q_i^\epsilon q_j^n + \dots$$



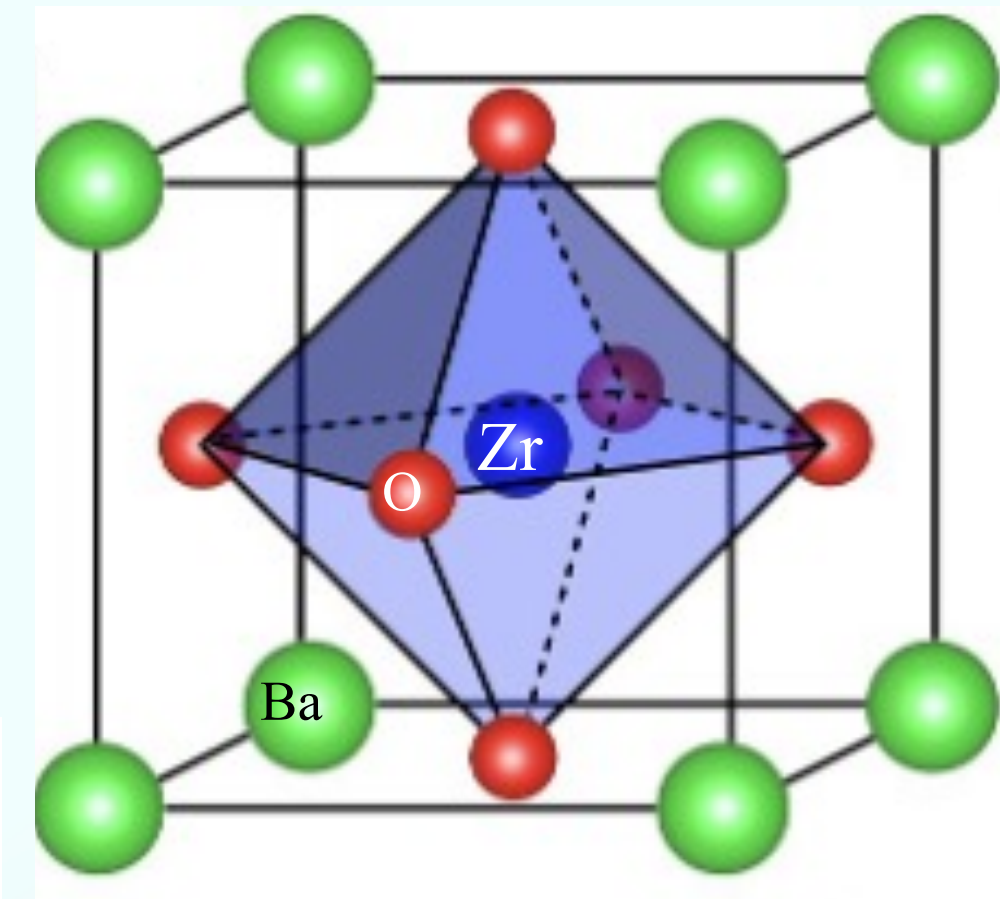
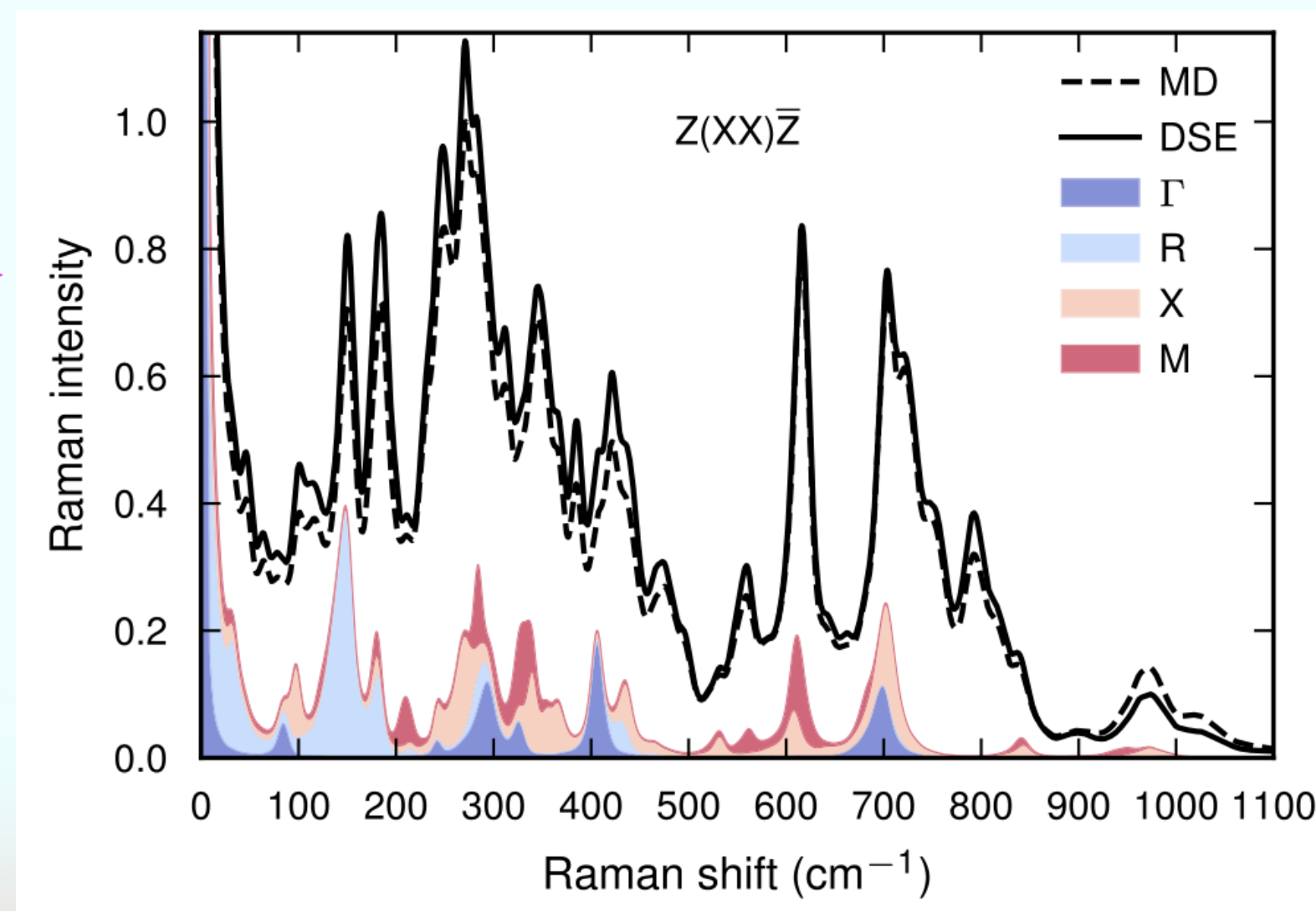
$$(R_i^\epsilon)_{\alpha\gamma} = \frac{\delta \chi_{\alpha\gamma}}{\delta q_i} \dots \longrightarrow \mathbf{0}$$

For Centro-symmetric Cubic System

$$(R_{ij\epsilon n})_{\alpha\gamma} = \frac{\delta^2 \chi_{\epsilon n}}{\delta q_i \delta q_j} \dots$$



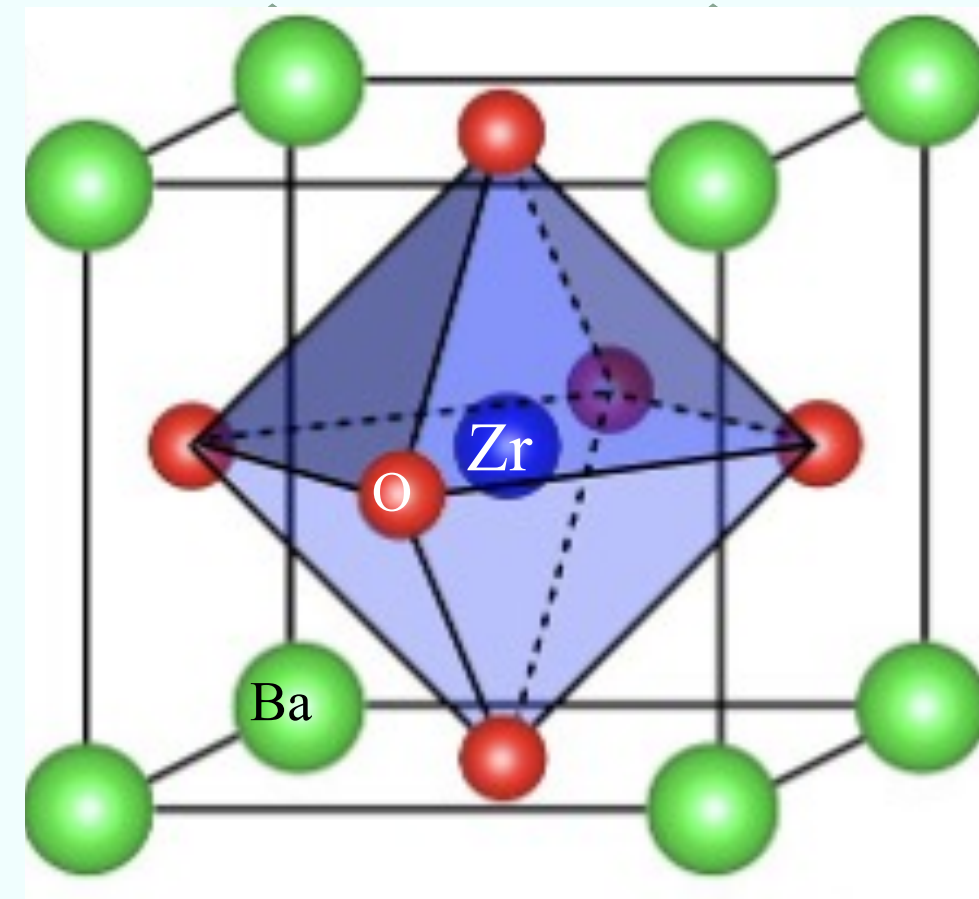
Source: Wikipedia



Cubic $pm\bar{3}m$

P. Rosander, et.al, *Phys. Rev. B* **111**, 064107 (2025)

Charged oxygen (anion) vacancy is responsible for such intense second order Raman signal at room temperature!



T Cubic $pm\bar{3}m$ n