Bachelor of Science in Materials and Metallurgical Engineering

HYDROTHERMAL SYNTHESIS AND CHARACTERIZATION OF PURE AND DOPED $BiVO_4$ NANOPARTICLES

Submitted by

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Backgrounds & Motivation

Water Splitting

- To generate H_2 as fuel

Photo – electrochemical Cells

- To reduce CO_2 to carbon based molecules

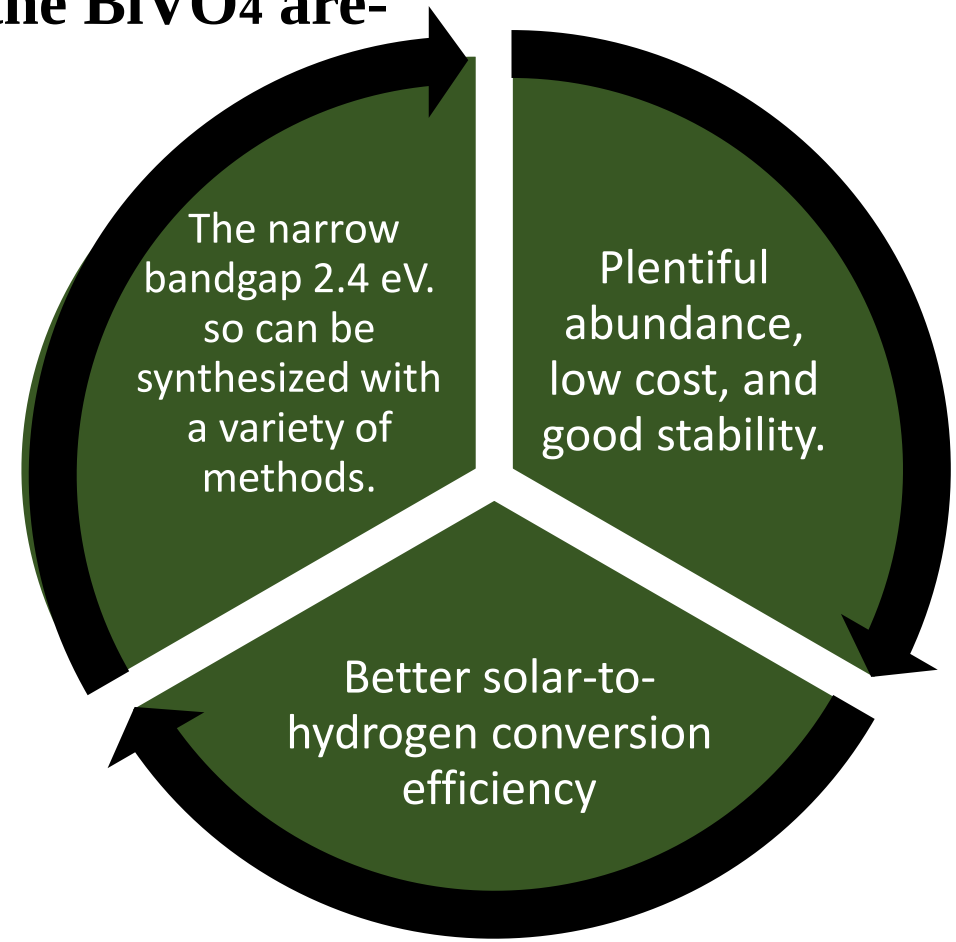
Photosynthesis

- To degrade pollutants responsible for water pollution
- Antibacterial activity in water

Need of a Photo – Active Material

Monoclinic $BiVO_4$ is one of the most promising visible-light-driven photocatalysts.

Reasons behind choosing the $BiVO_4$ are-



Targets and Challenges of this Research

- ❖ Effect of the addition of K_2SO_4 as morphology controlling agent on formation of monoclinic – tetragonal heterostructured BiVO4.

- ❖ Effect of Nd doping at Bi $^{3+}$ sites on structural formation, optical bandgap and particle morphology.

- ❖ Effect of Mn doping at V $^{5+}$ sites on structural formation, optical bandgap and particle morphology

Crystal Structure of $BiVO_4$

Naturally found as the mineral pucherite with an orthorhombic crystal structure.

Laboratory synthesis crystallizes either in a scheelite or a zircon-type structure.

- Scheelite type structure
  - **Monoclinic** (space group *I2*/b with a = 5.1935 A^o, b = 5.0898 A^o, c = 11.6972 A^o, β = 90.387^o)
  - **Tetragonal** (space group $I4_1$/a with a = b = 5.1470 A^o, c = 11.7216 A^o)

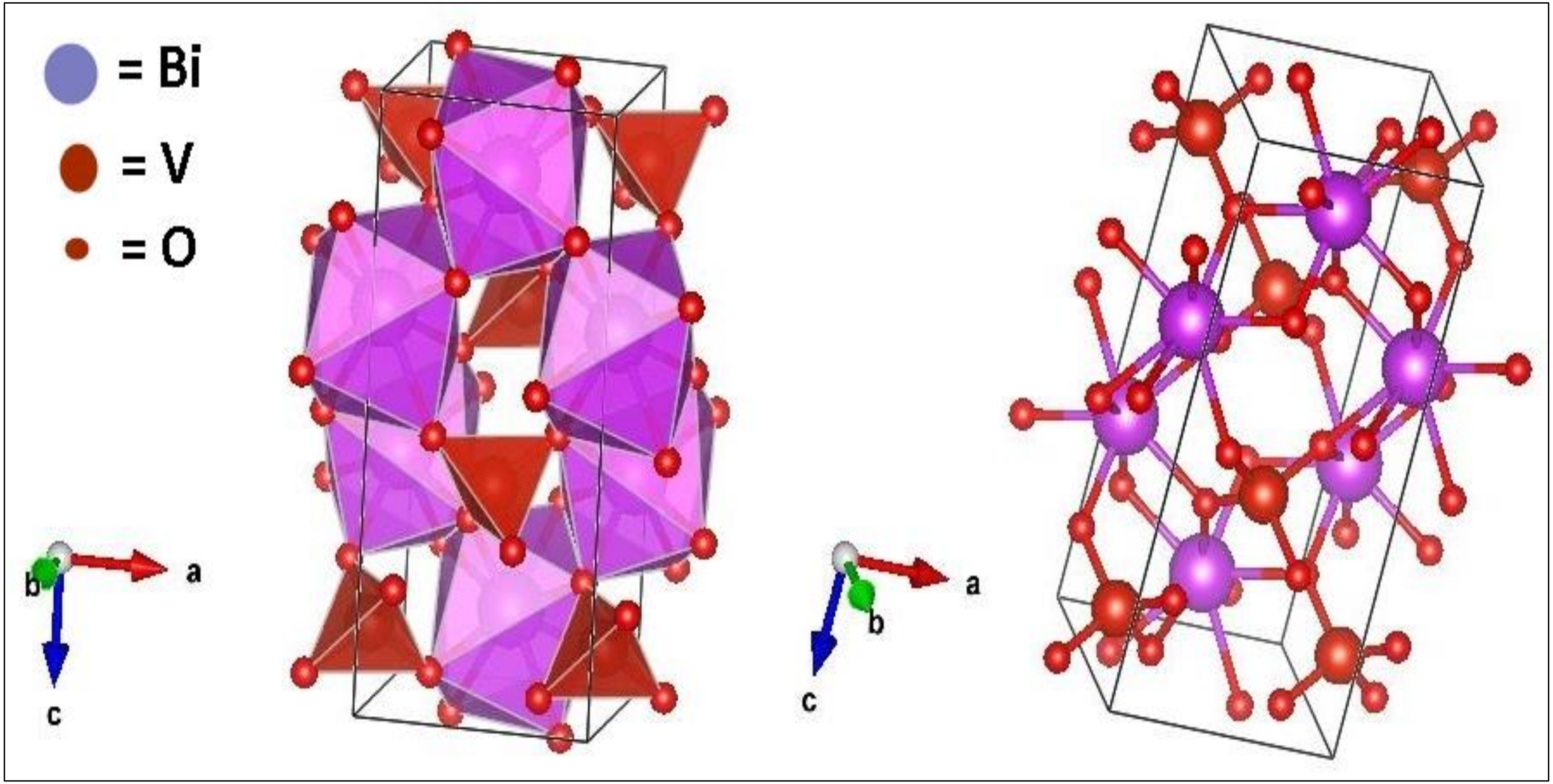
- Zircon type structure
  - **Tetragonal** (space group $I4_1$/a with a = b = 7.303 A^o, c = 6.584 A^o)

Crystal Structure of $BiVO_4$

- Difference between scheelite type tetragonal and zircon type tetragonal structure: **Lattice parameter**

- Difference between scheelite type tetragonal and scheelite type monoclinic structure: **Distortion**

Crystal Structure of $BiVO_4$



Crystal Structure of $BiVO_4$

- Each V ion is coordinated by four O atoms in a tetrahedral site and each Bi ion is coordinated by eight O atoms from eight different VO4 tetrahedral units

- Each O atom in this structure is coordinated to two Bi centers and one V center, holding the Bi and V centers together forming a three dimensional structure.

- The only difference between the tetragonal and monoclinic scheelite structure is that the local environments of V and Bi ions are more significantly distorted in the monoclinic structure, which removes the four-fold symmetry necessary for a tetragonal system.

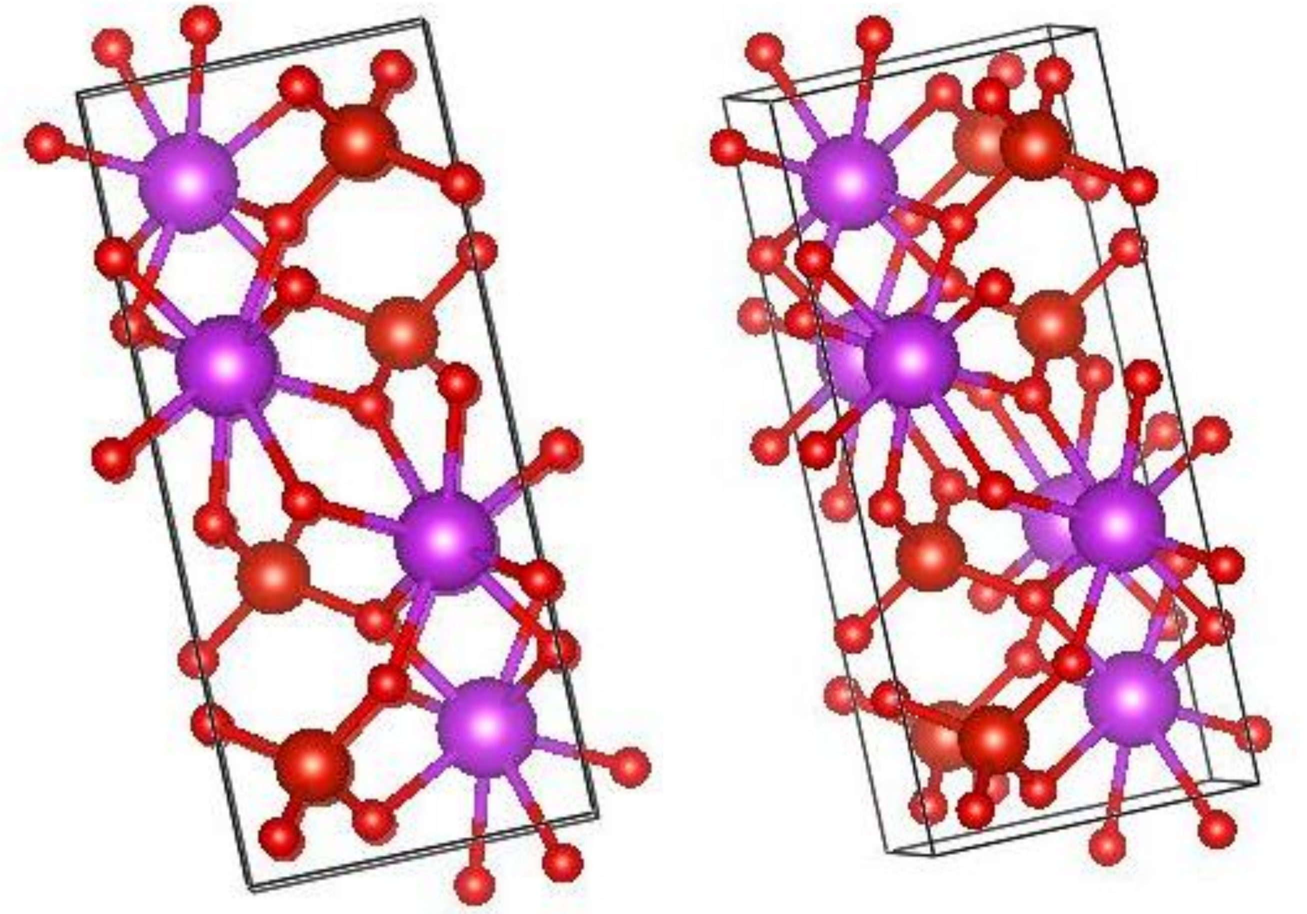
2 Fold Symmetry of $BiVO_4$

Bi has 4 identical (Bi – O) bond

V has 2 identical (V – O) bond

Tetragonal: All identical bonds are equal. No distortion.

Monoclinic: Identical bonds are not equal. Distortion occurs in the structure.



It becomes easier for electron to transfer from Bismuth than oxygen to V.

Electron Transfer in $BiVO_4$

Goal:
Reduced bandgap in m – BVO

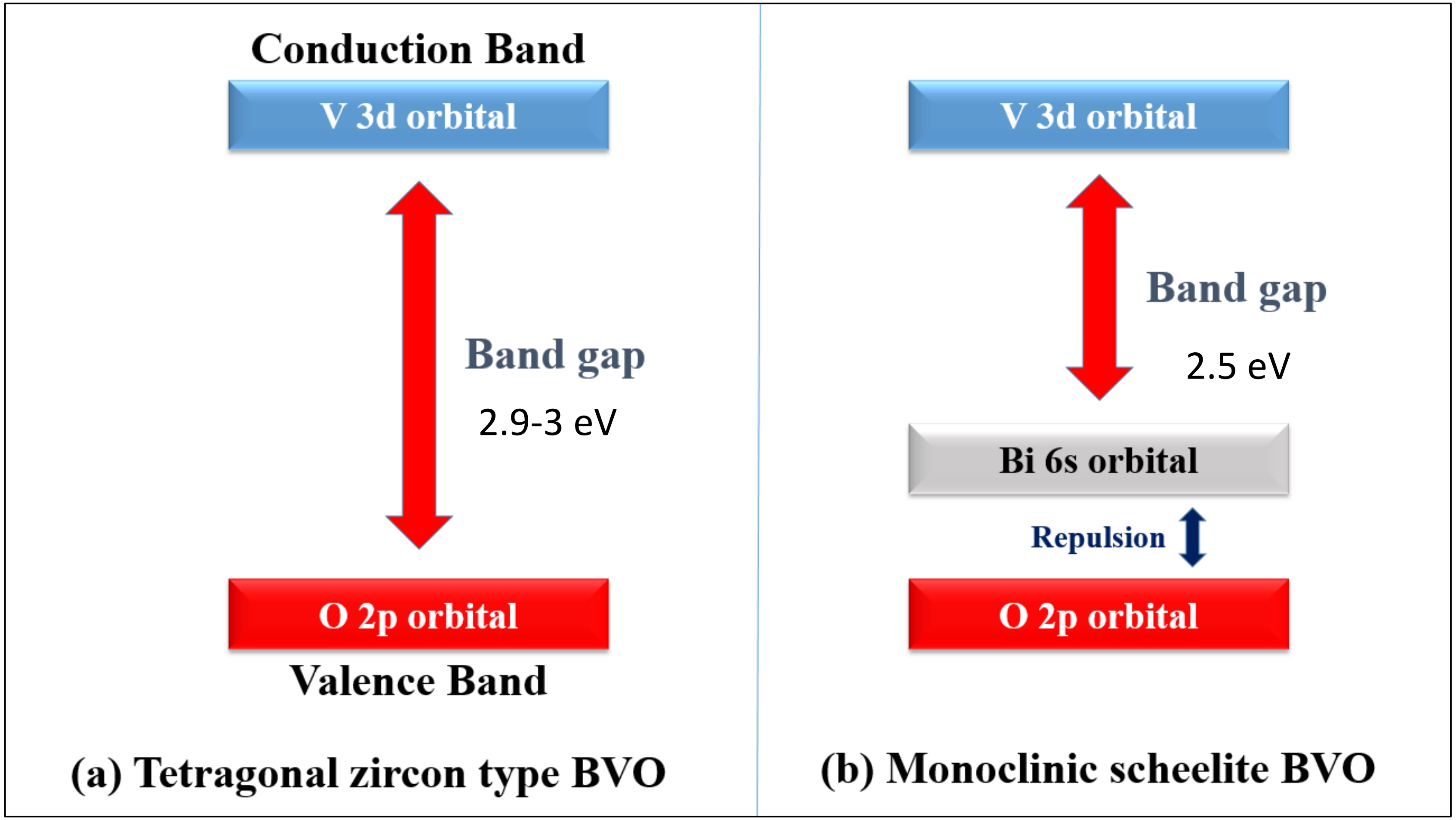
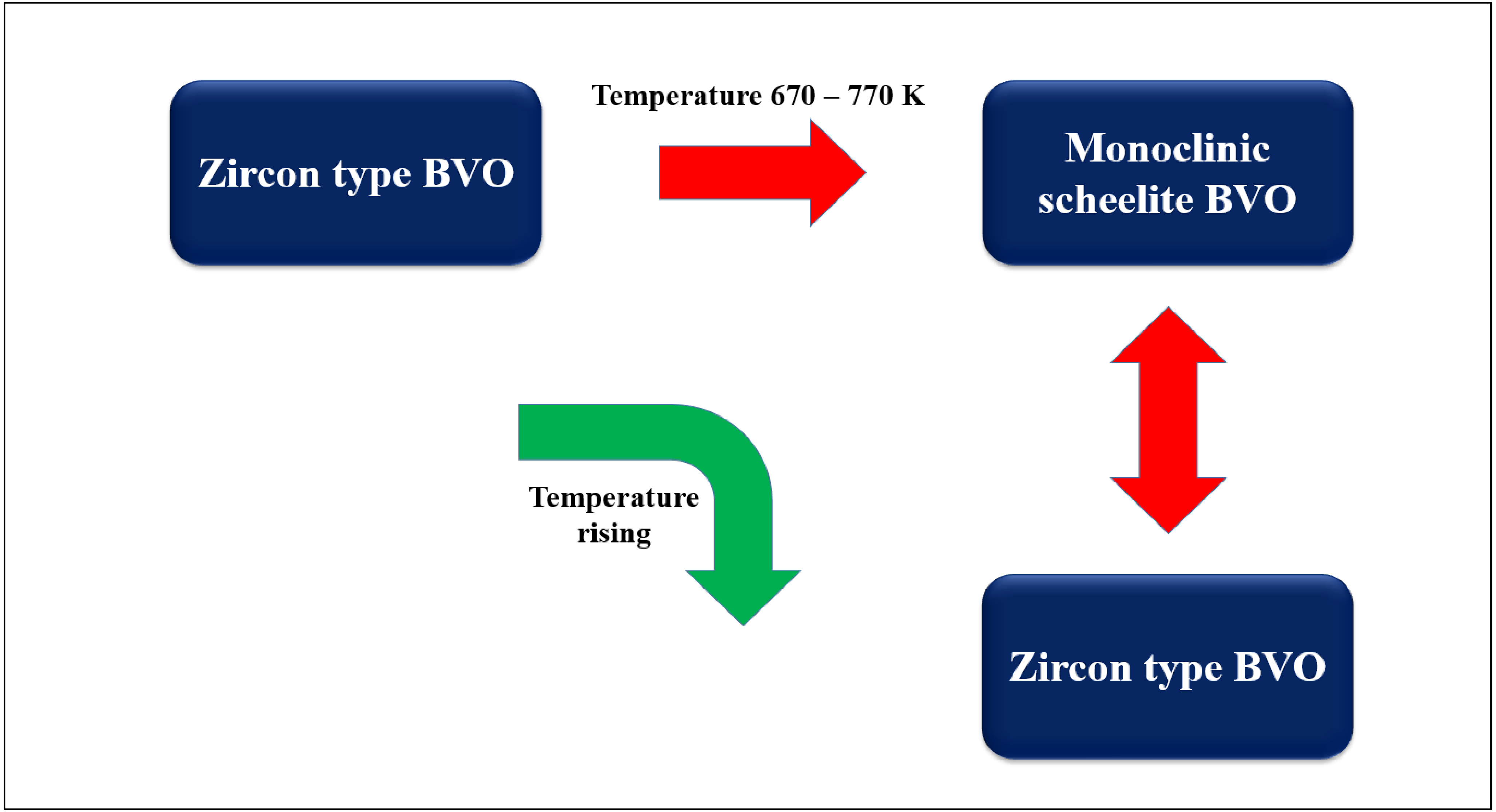


Fig: Schematic diagram explaining the bandgap reduction in m – BVO

Transformation of $BiVO_4$ Phases with T



Transformation of $BiVO_4$ Phases with T

- Previous studies say that **low temperature synthesis** always tends to form tetragonal zircon type BVO [3]

- If temperature is raised more, **irreversible transformation** of phases from zircon type tetragonal to monoclinic scheelite BVO will take place at 670-770 K.

- However, if temperature is kept increasing, **reversible transformation** of monoclinic scheelite BVO to tetragonal scheelite BVO will take place.

Reasons for Hydrothermal Synthesis

Pressure in hydrothermal is above 200 kbar at 200 degree C.

Due to this high pressure, T required for m – BVO is reduced & m – BVO can be found in low temperature synthesis.

Two major advantages:

- Increased T causes less crystalline BVO, low T synthesis is preferred
- Hydrothermal synthesis environment is well protected by Teflon lined Stainless Steel autoclave

Preparative Parameters of Synthesized Samples of $BiVO_4$

Sample No	Sample	Precursor	Molar Amount	Weight	Temperature
BVO S1	$BiVO_4$	$Bi(NO_3)_3.5H_2O$ V_2O_5 H_2O	0.2 mmol 0.2 mmol	97 mg 36.38 mg 10 mL	200 ^{0}C
BVO S2	$BiVO_4$	$Bi(NO_3)_3.5H_2O$ V_2O_5 K_2SO_4 H_2O	0.2 mmol 0.2 mmol 5.7 mmol	97 mg 36.38 mg 1 gm 10 mL	200 ^{0}C
BVO S3	$Bi_{0.9}Nd_{0.1}VO_4$	$Bi(NO_3)_3.5H_2O$ Nd_2O_5 V_2O_5 K_2SO_4 H_2O	0.18 mmol 0.01 mmol 0.2 mmol 5.7 mmol	87.3 mg 3.68 mg 36.38 mg 1 gm 10 mL	200 ^{0}C
BVO S4	$BiV_{0.9}Mn_{0.1}O_4$	$Bi(NO_3)_3.5H_2O$ V_2O_5 $Mn(NO_3)_2.4H_2O$ K_2SO_4 H_2O	0.2 mmol 0.18 mmol 0.01 mmol 5.7 mmol	97 mg 32.742 mg 25.101 mg 1 gm 10 mL	200 ^{0}C

Precursor

- $Bi(NO_3)_3$: Provides Bi^{3+}. Soluble in room temperature

- V_2O_5: Provides VO_3 ion. The more VO_3 ion, the more **$BiVO_4$**

- Addition of K_2SO_4:

  - Formation of **pure m - $BiVO_4$** with a slight % tetragonal zircon type $BiVO_4$ phase

  - **No impurity (Bi_2O_3) phase**

Doping Materials – Nd

- Nd has larger atomic radius (245 pm) than Bi (230 pm)
- Doping of 10% Nd replacing Bi at dodecahedral site
- Due to larger atomic radius, Nd has been chosen to investigate if any distortion takes place
- Nd = [Xe] $6s^2$ $4f^4$. Nd^{3+} has no lone pair like Bi^{3+}

Doping Materials – Mn

- Mn has multi valence state (3+, 4+ & 5+) & strong interaction with Oxygen

- Tetrahedral site has smaller volume than dodecahedral

- 10% Mn doping has been chosen to investigate if any distortion takes place

Synthesis Process

- Measurements
- Heating & Stirring
- Heating in autoclave
- Centrifugation
- Drying & Collecting

Characterization

Phase Study + **Rietveld Refinement**

Microstructures Analysis (SEM)

UV – Vis Analysis

$BiVO_4$ without K_2SO_4 = **BVO S1**

$BiVO_4$ with K_2SO_4 = **BVO S2**

$Bi_{0.9}Nd_{0.1}VO_4$ = **BVO S3**

$BiMn_{0.1}V_{0.9}O_4$ = **BVO S4**

Phase Study

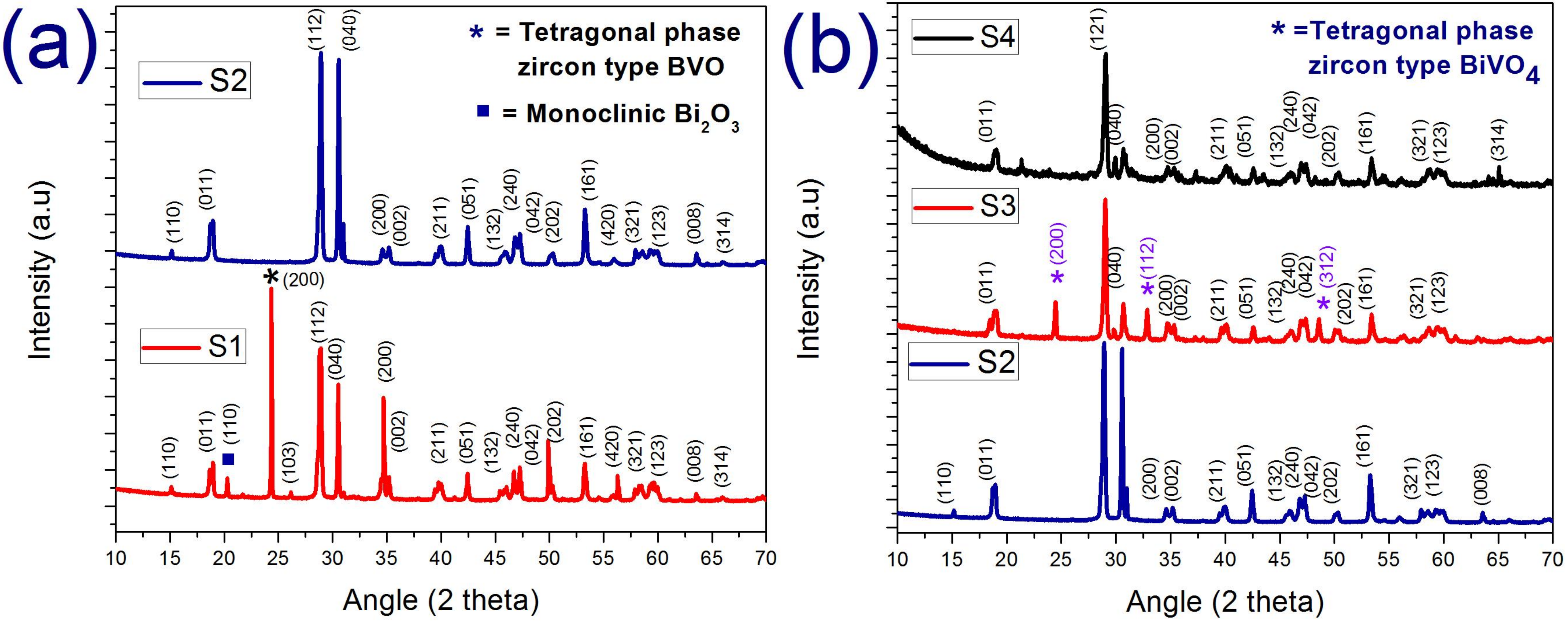


Fig: XRD Patterns of (a) BVO S1 & BVO S2 (b) BVO S2, BVO S3 and BVO S4

Phase Study

How to identify the peaks?

With the help of previous studies published in journals???

What if some peaks remain unidentified and unmatched!!

Rietveld Refinement Analysis

Bragg reflections of pure phases obtained from Crystallographic Open Database

Simulation

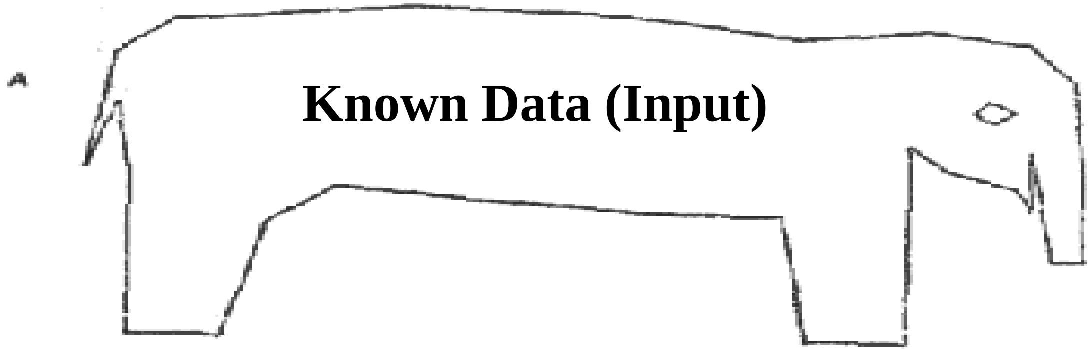
Chi Square Goodness Fitting

Non-linear Curve Fitting

Experimental XRD pattern data

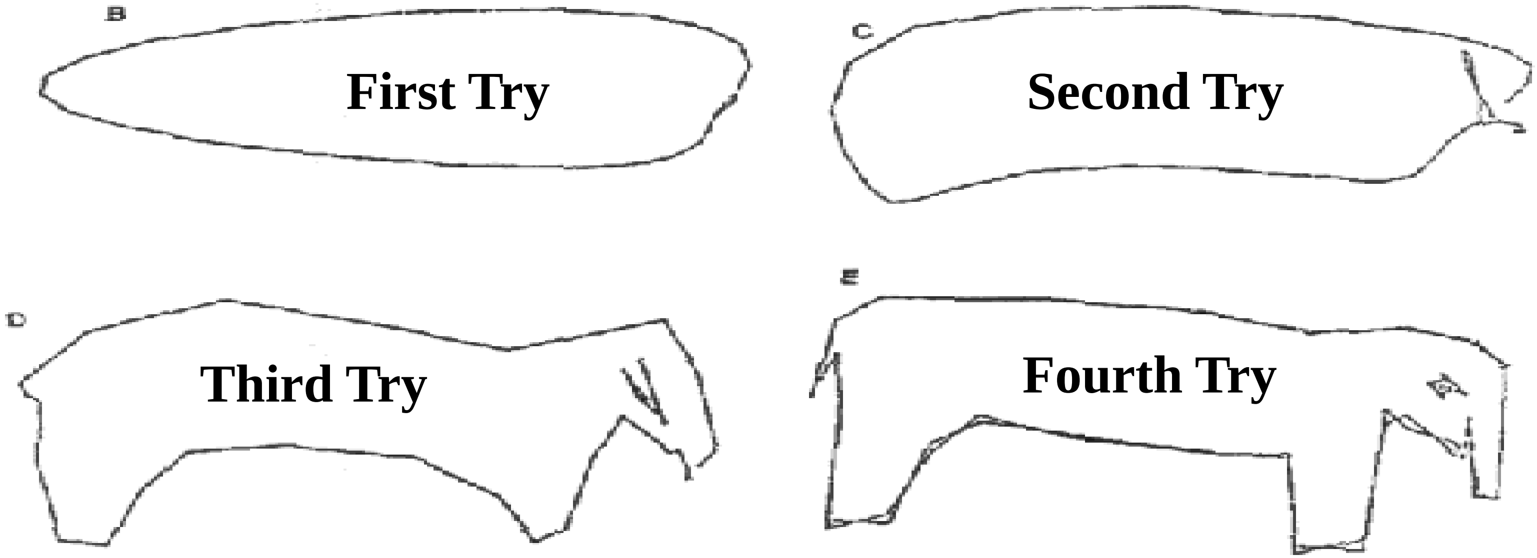
Rietveld Refinement Analysis

How Rietveld Refinement draws an elephant by own



Machine Learning

like **iOS Prisma app** or Google's "deep – learning"



Rietveld Refinement Analysis

The main principle is to calculate intensity at point i of the diagram:

$$y_{ic} = y_{ib} + \sum_{\Phi} S_{\Phi} \sum_{k} G_{\Phi}(2\theta_i - 2\theta_k) I_k$$

Intensity of Bragg Reflections

$$I_k = m_k L_k |F_k|^2 P_k A_k$$

Goal is to minimize this residual function ➡

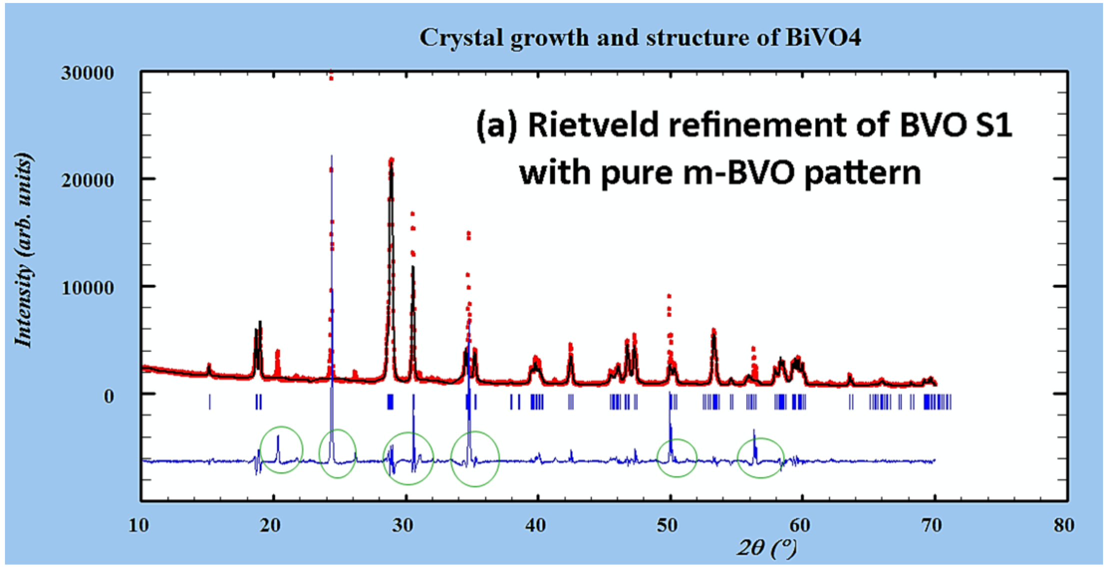
$$\sum_i w_i \left(y_i^{obs} - y_i^{calc} \right)^2$$

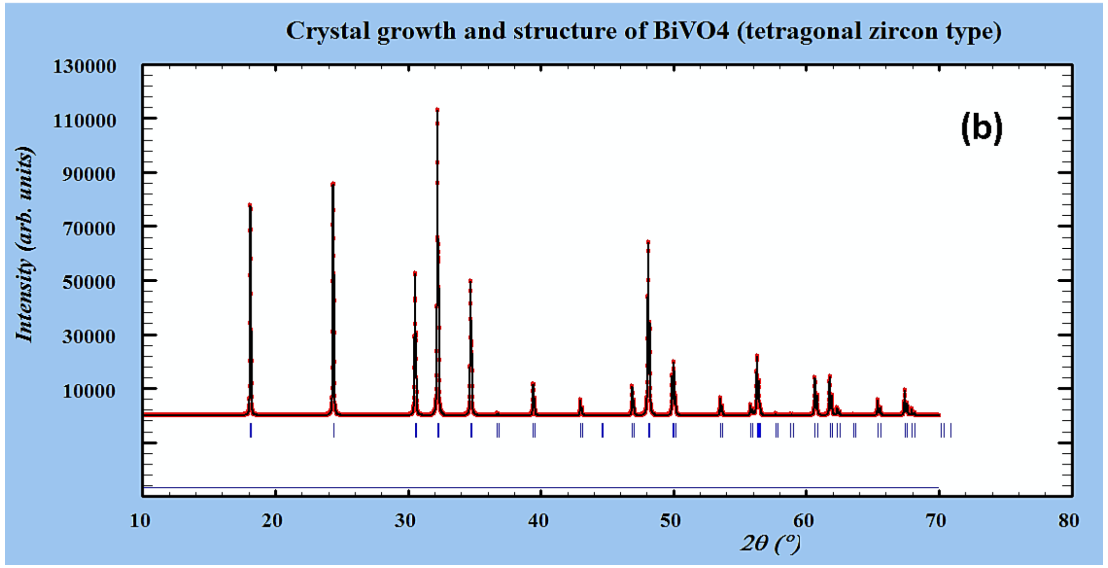
where $w_i = 1/y_i^{obs}$

y_i^{obs}: observed intensity at the ith step

y_i^{calc}: calculated intensity at the ith step

Rietveld Refinement of BVO S1



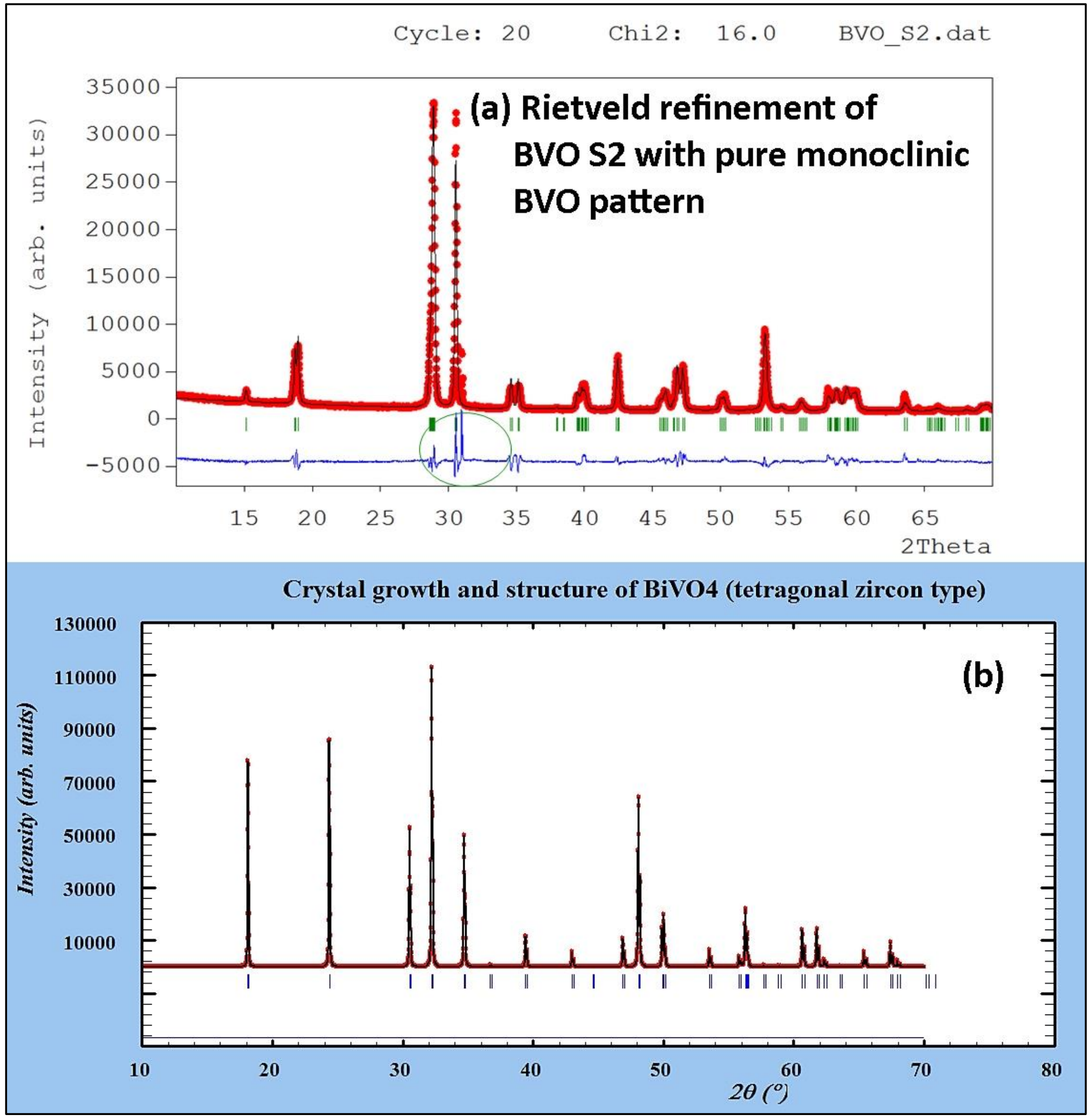


Refinement was performed with pure m – BVO
And unmatched reflections are compared with pure tetragonal zircon type BVO

Reflections unmatched with pure m – BVO:
2 theta = 20.5, 24.5, 31, 50, 56.5

Except reflection at 2 theta = 20.5,
All other unmatched reflections match with tetragonal zircon type BVO

Rietveld Refinement of BVO S2



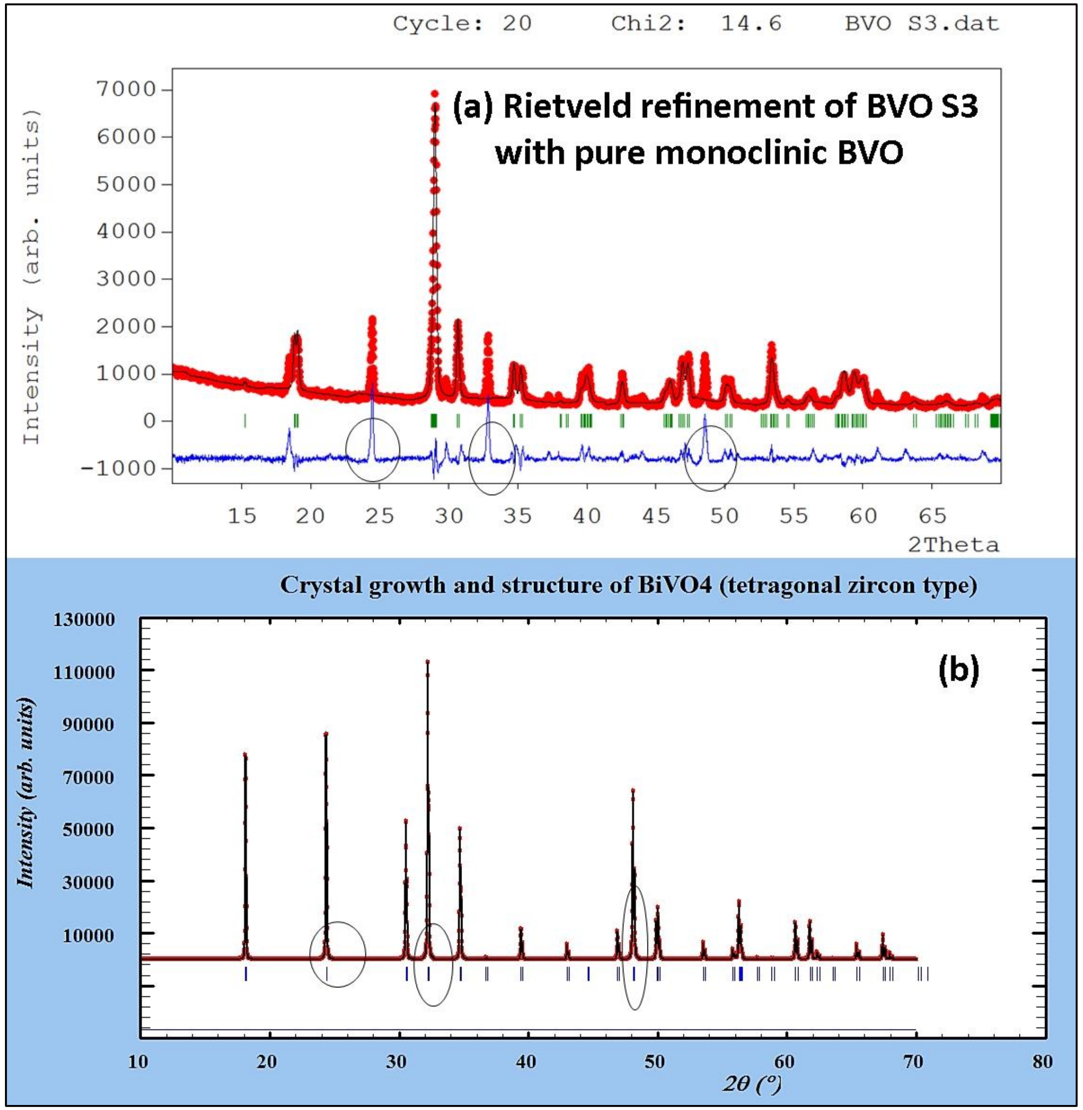
Refinement was performed with pure m – BVO

And unmatched reflections are compared with pure tetragonal zircon type BVO

A slight difference was noticed at 2 theta = 31

BVO S2 = Pure monoclinic BVO

Rietveld Refinement of BVO S3



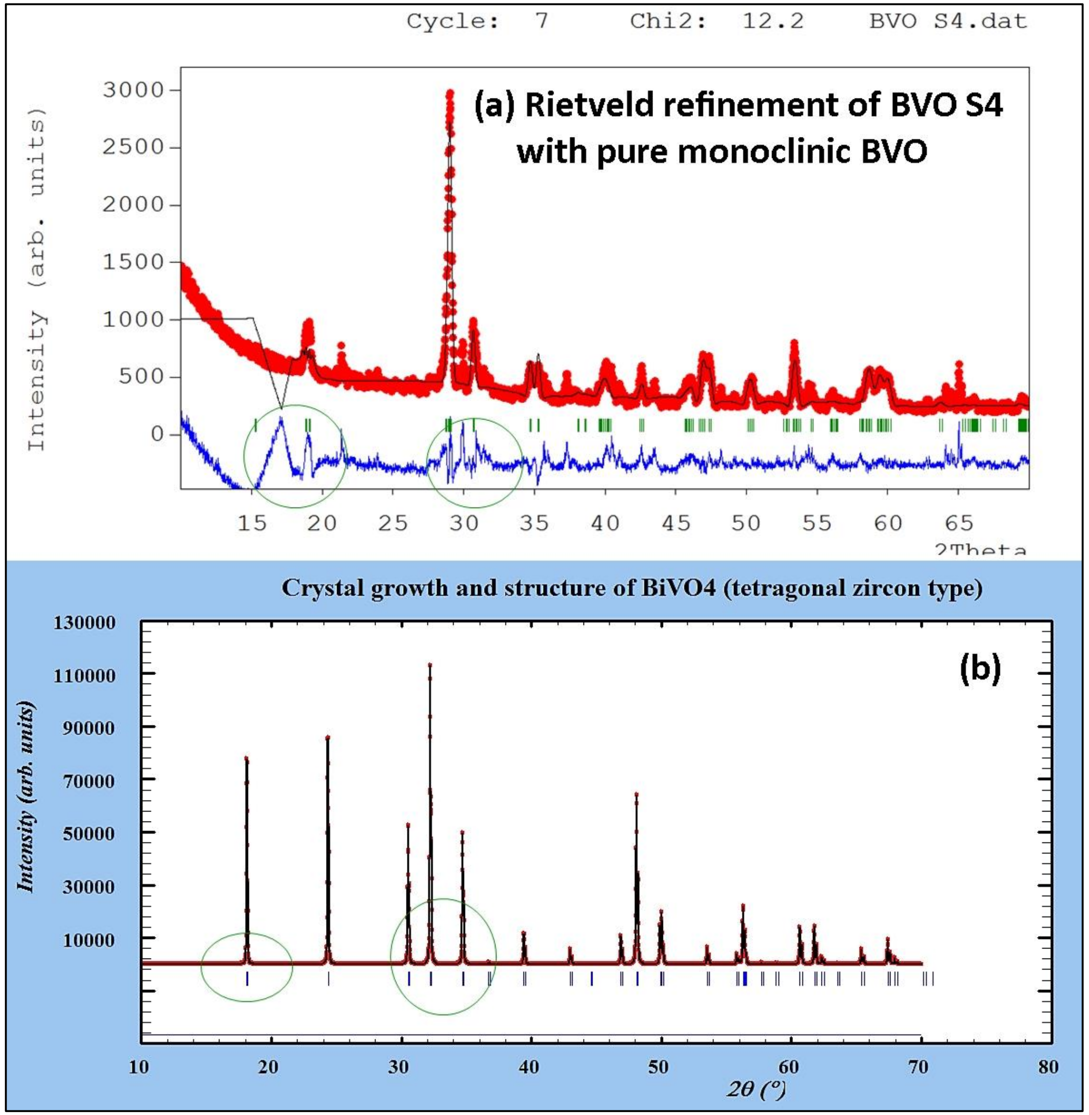
Refinement was performed with pure m – BVO

And unmatched reflections are compared with pure tetragonal zircon type BVO

Reflections unmatched with pure m – BVO:
2 theta = 24.5, 33, 48

% tetragonal phase increased than BVO S2
And
No impure phases

Rietveld Refinement of BVO S4

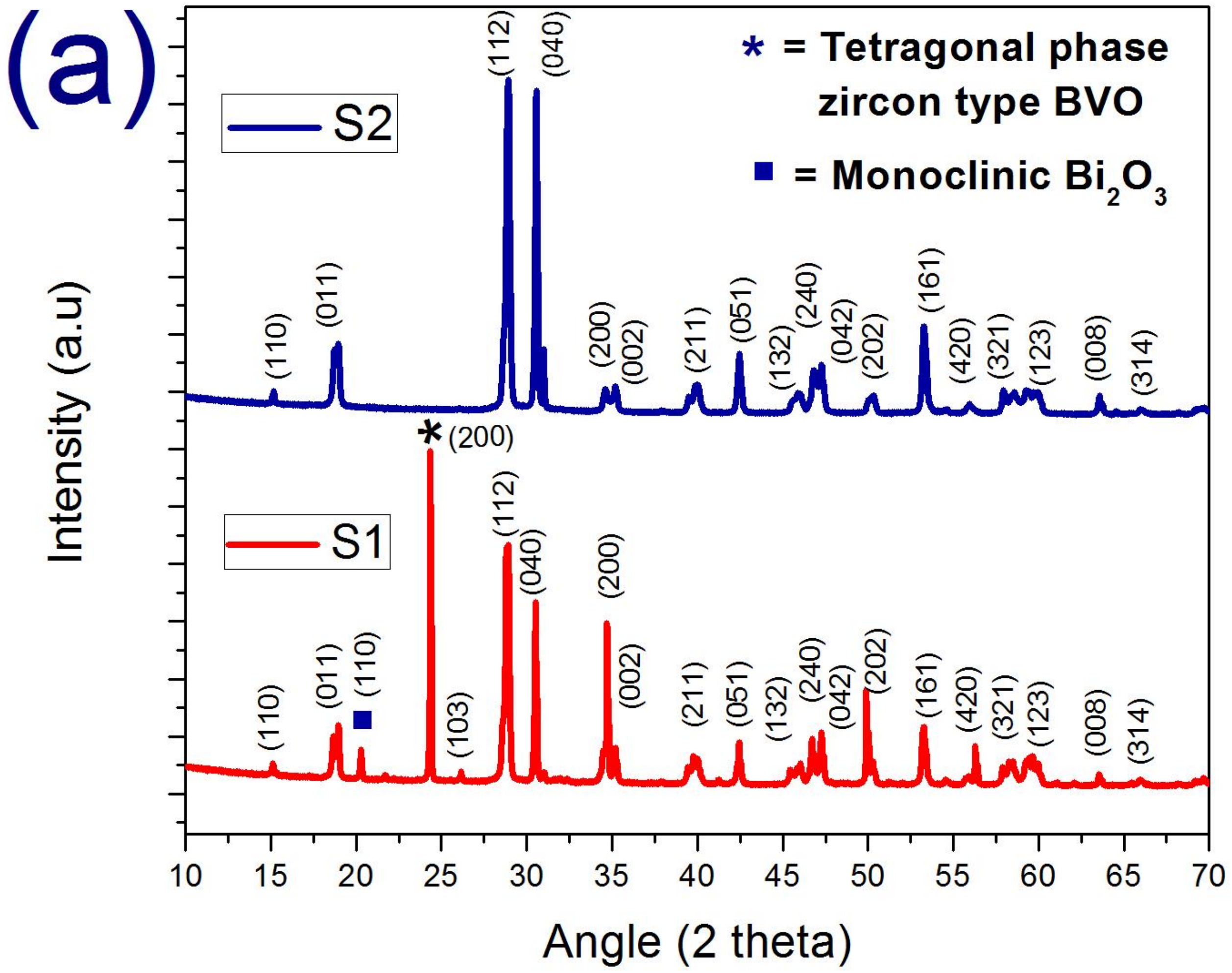


Refinement was performed with pure m – BVO
And unmatched reflections are compared with pure tetragonal zircon type BVO

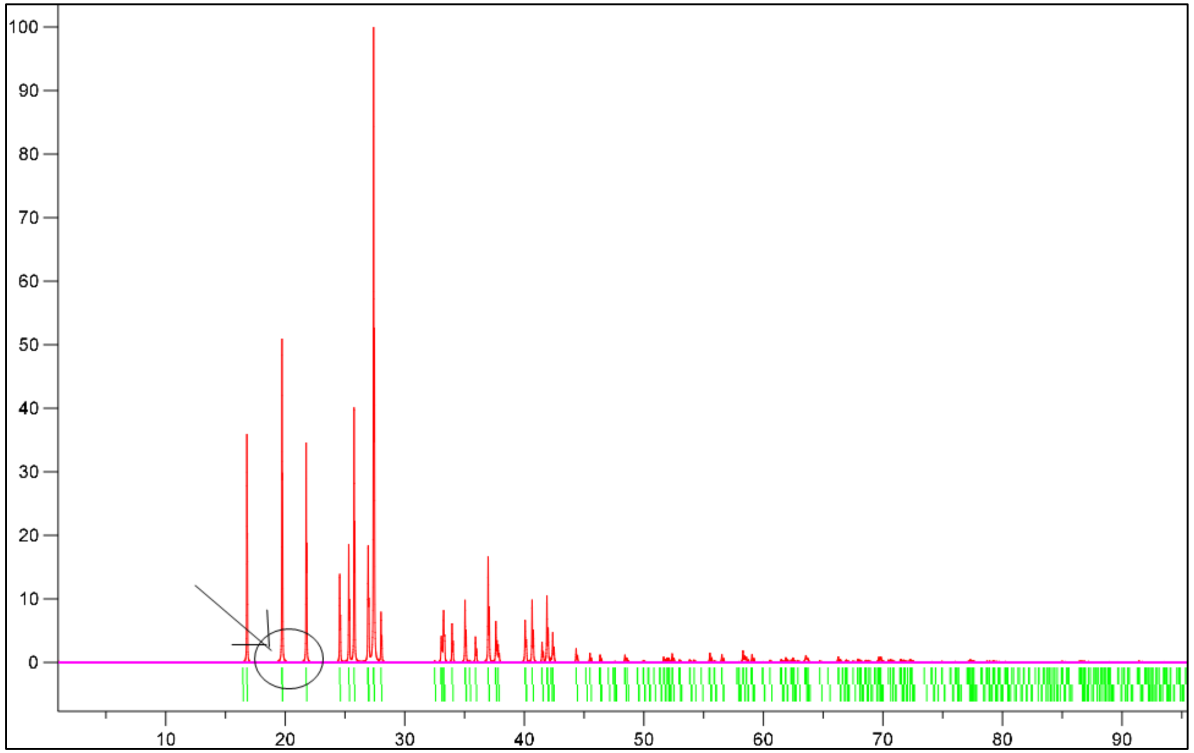
Difference is for improper centrifugation During synthesis

BVO S4 = Almost pure m - BVO

Presence of Bi_2O_3 in BVO S1

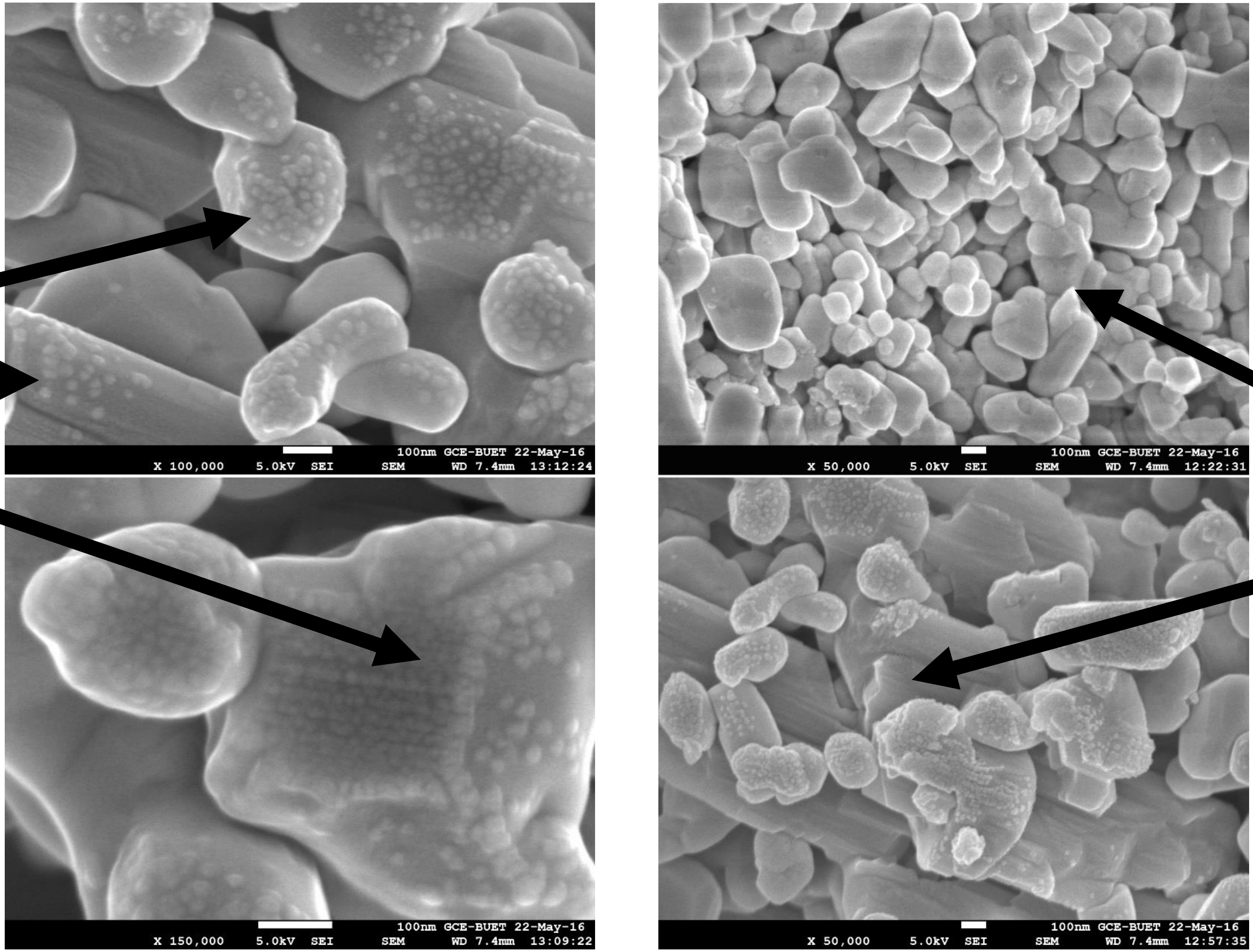


XRD Pattern of pure Bi_2O_3 (monoclinic)



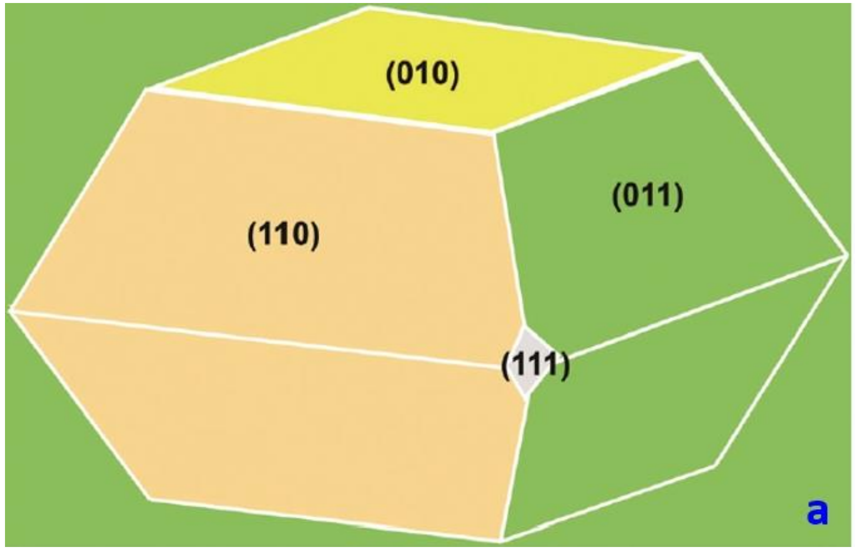
SEM Images of BVO S1

Impurity phase Bi_2O_3

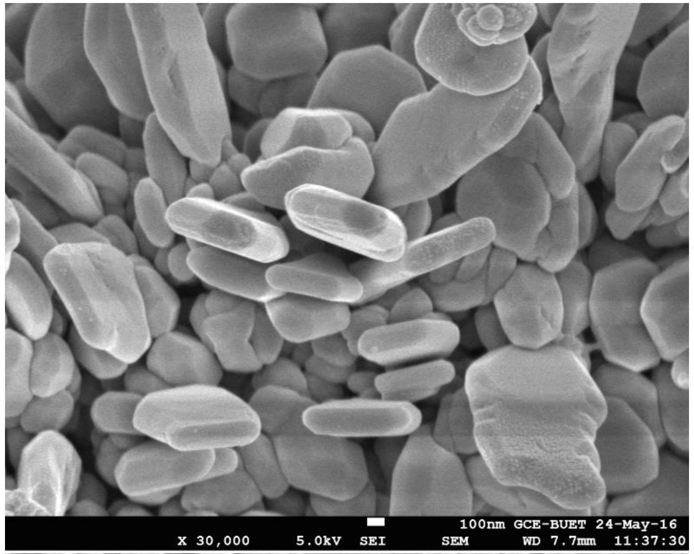


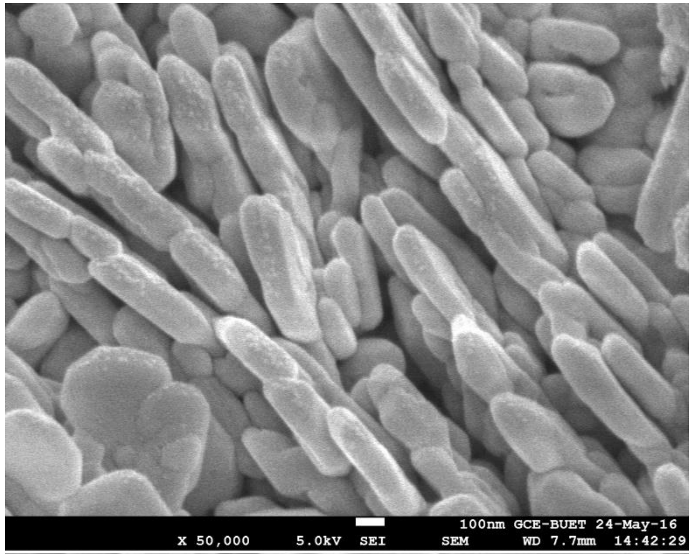
Non – uniform Size distribution

SEM Images of BVO S2

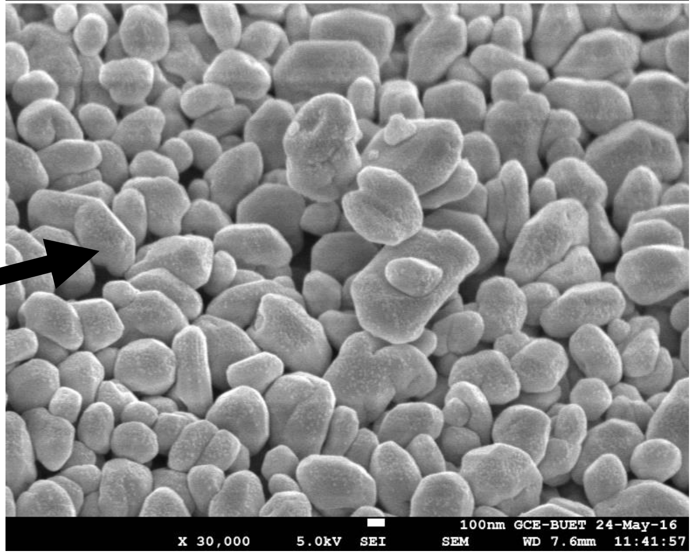


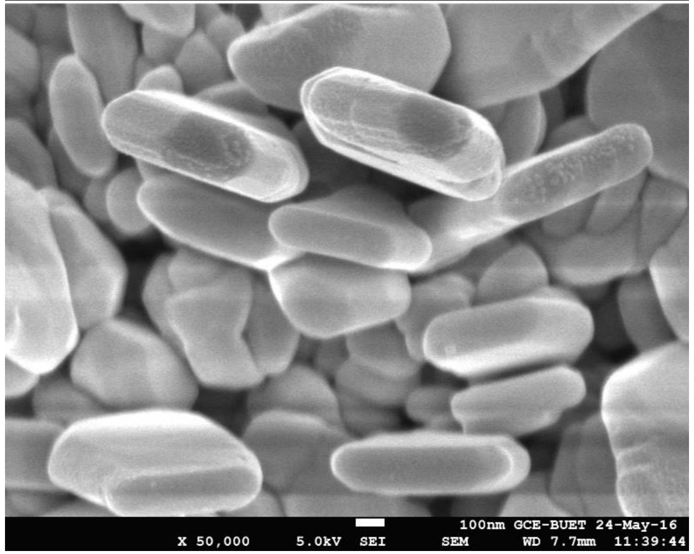
Pellet shapes BVO



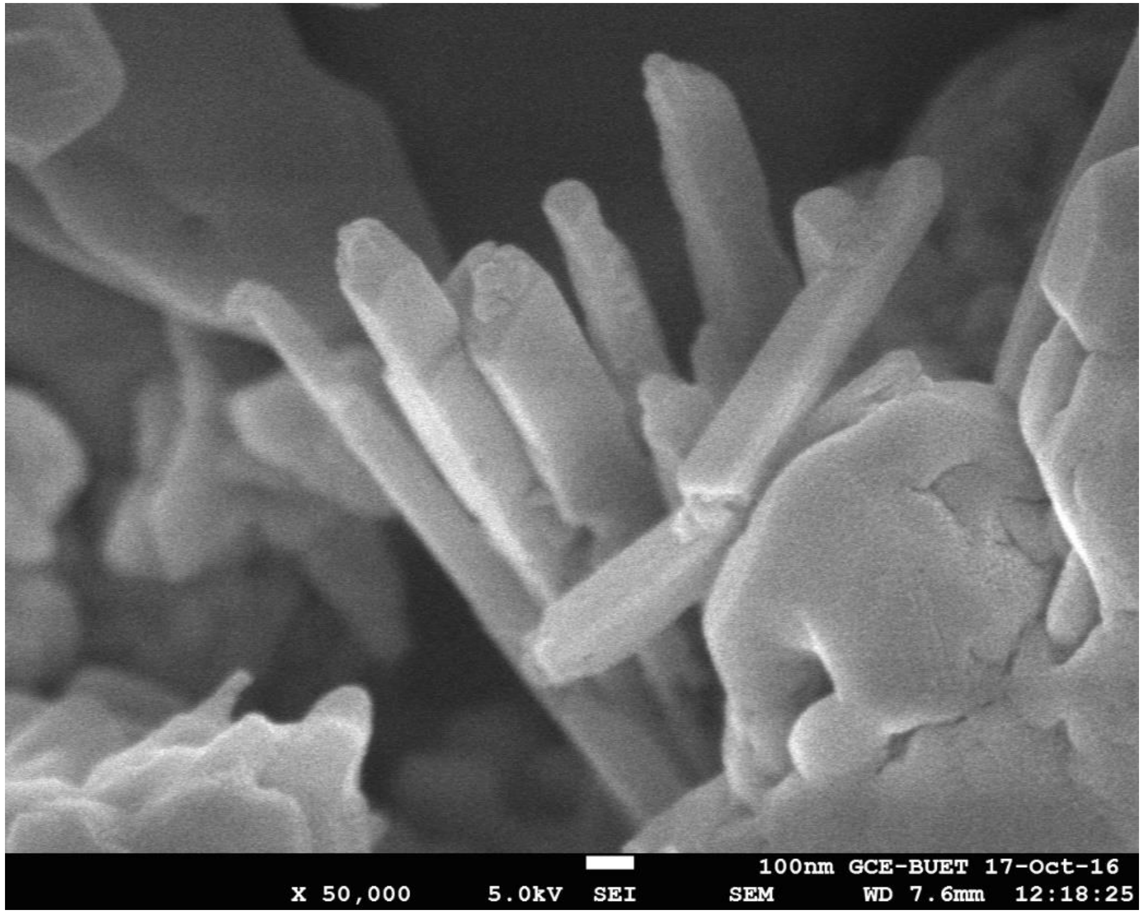


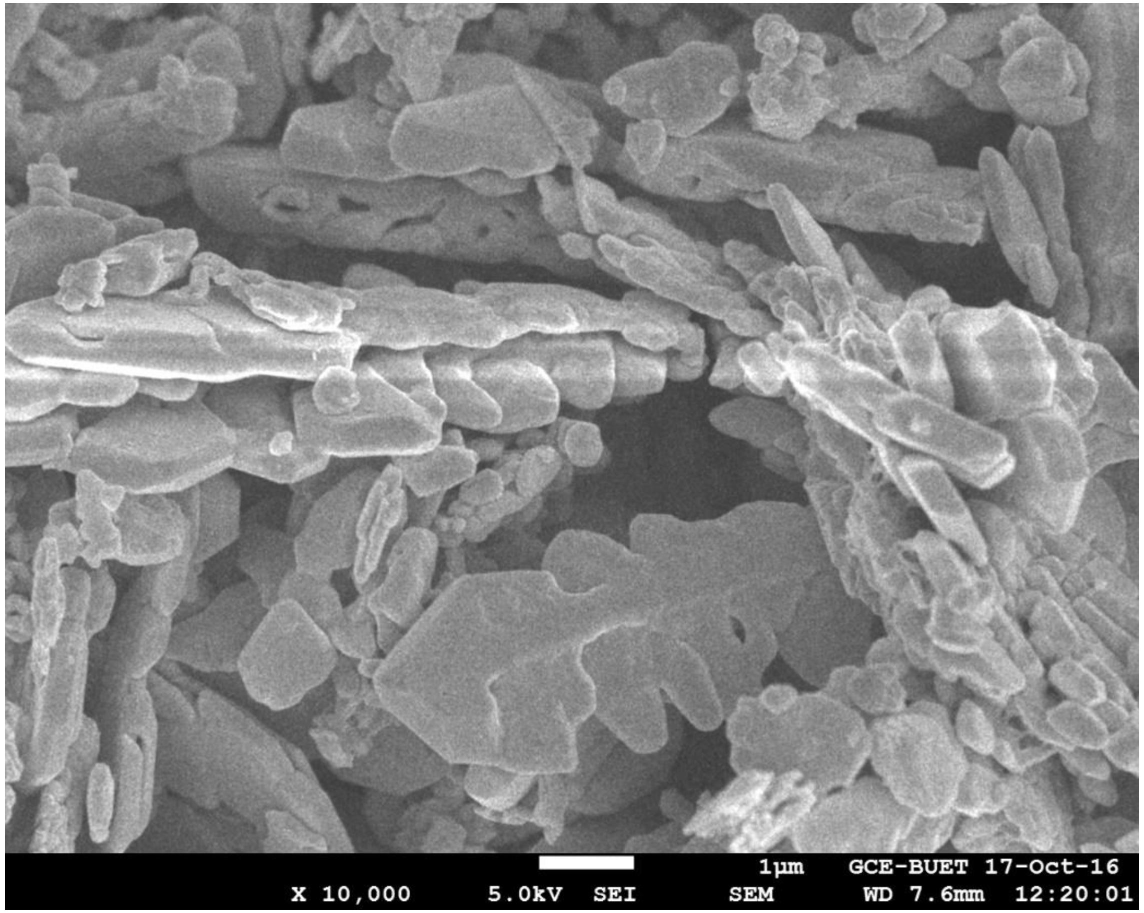
Uniform Size distribution



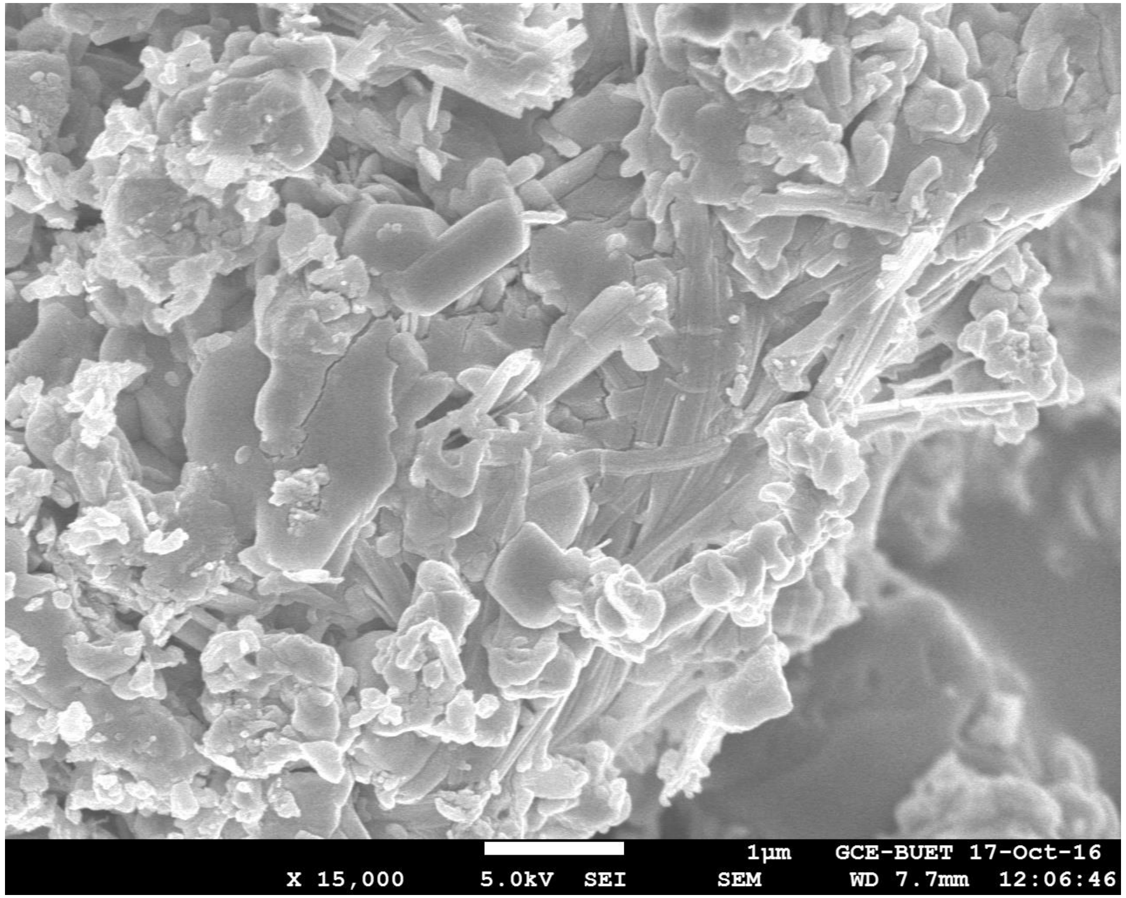


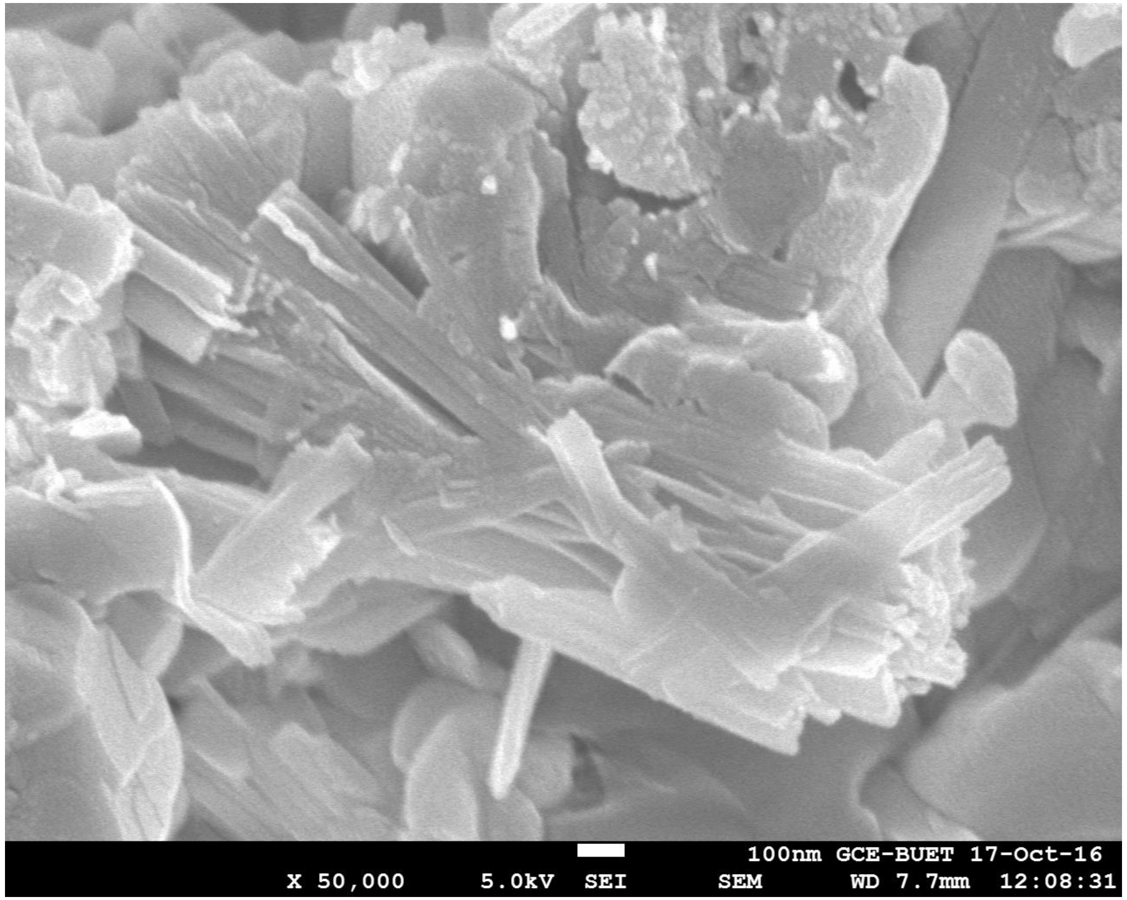
SEM Images of BVO S3



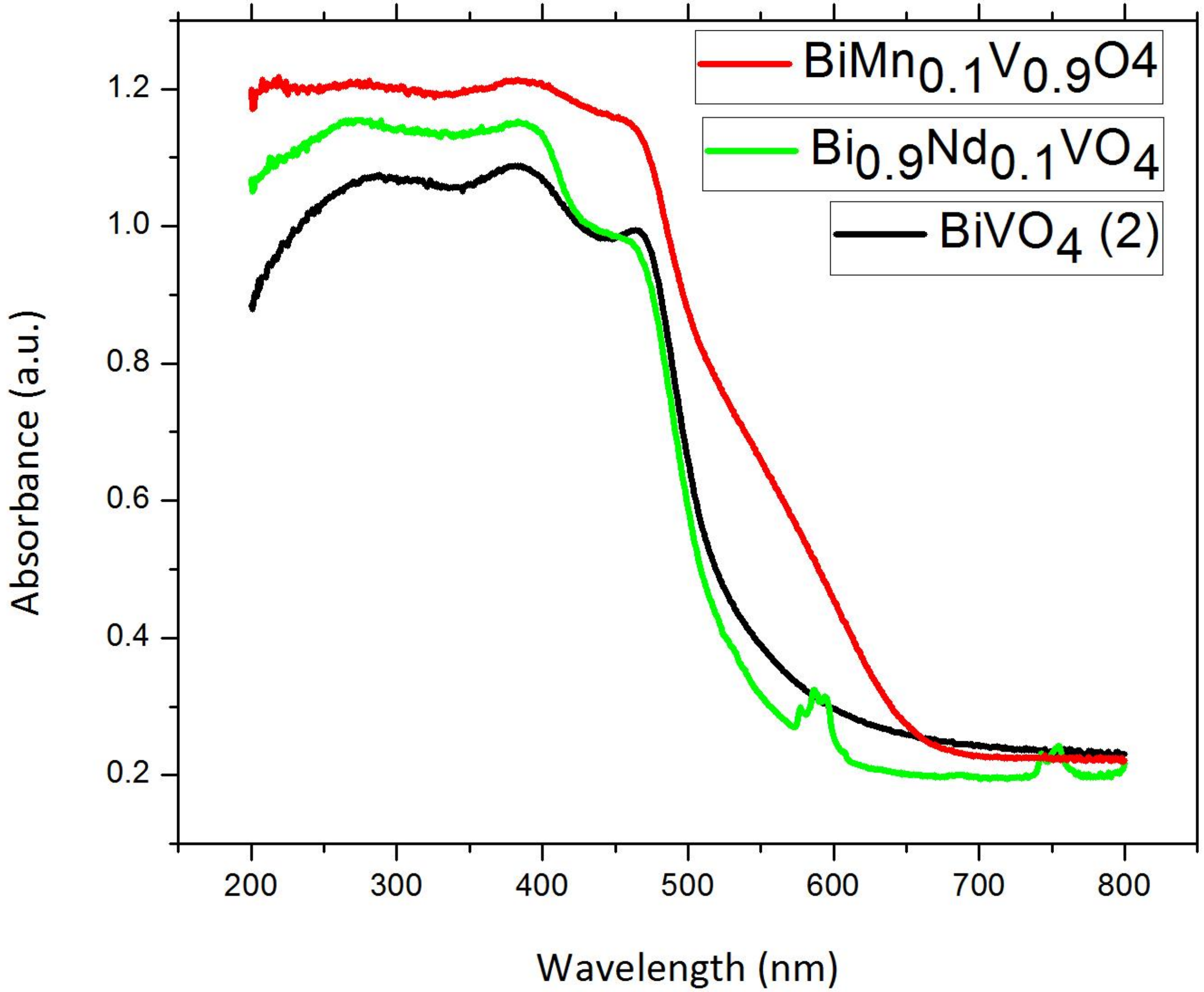


SEM Images of BVO S4





UV – Vis Analysis



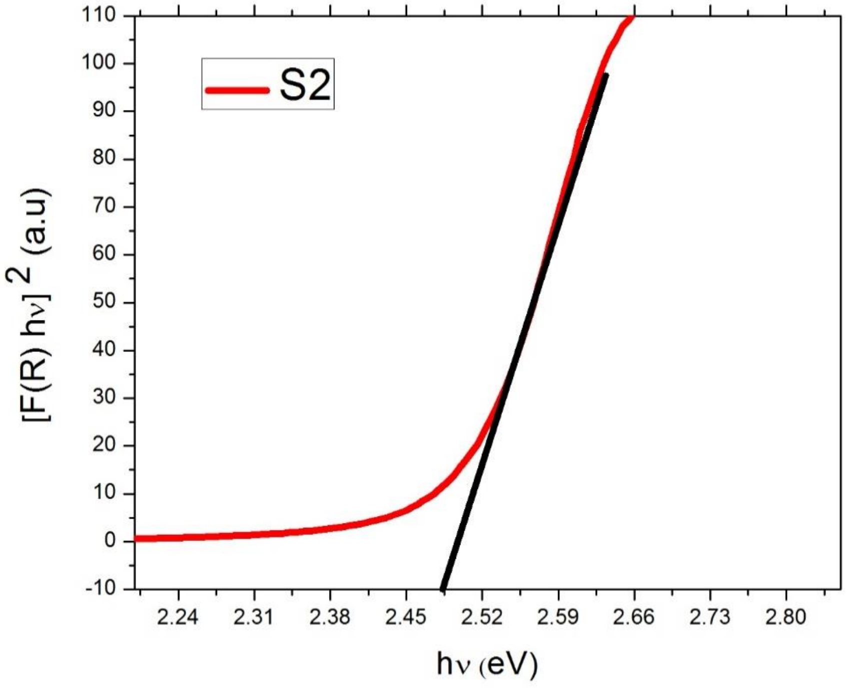
The fall of the curves within 400 – 500 nm indicates that all three synthesized particles will be active in visible range.

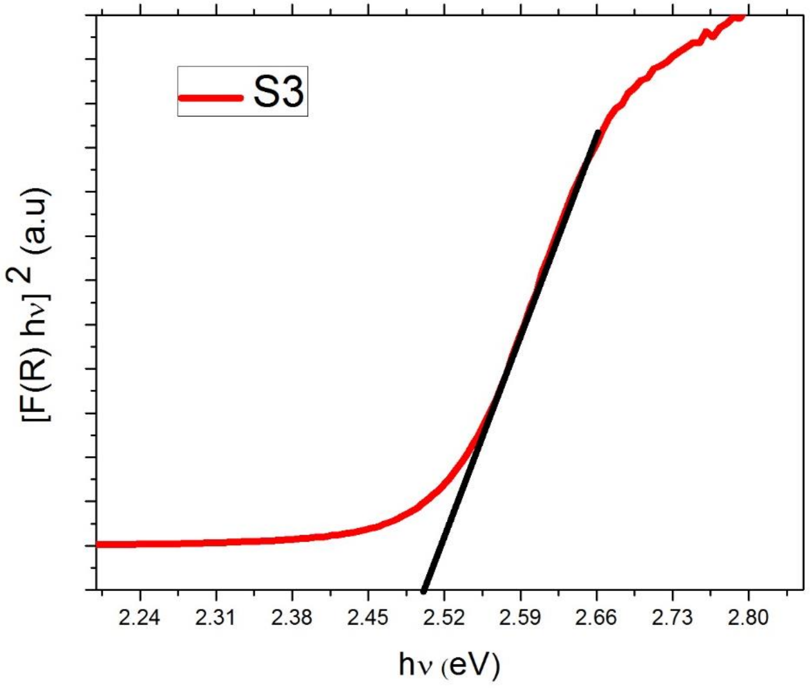
UV – Vis Analysis

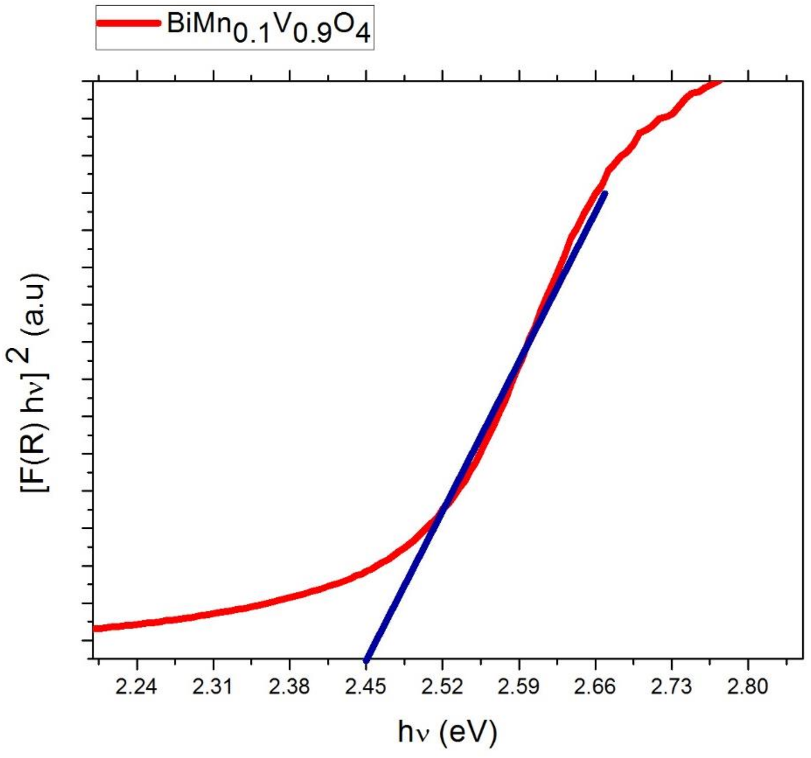
$$F(R) = \frac{(1-R)^2}{2R} \text{ ----------- (1)}$$

Bandgap is calculated using Kubelka – Munk function (1)

[hνF(R)] ²vs photon energy (hν) plots







BVO S2 = 2.49 eV **BVO S3 = 2.5 eV** **BVO S4 = 2.44 eV**

Results & Discussions

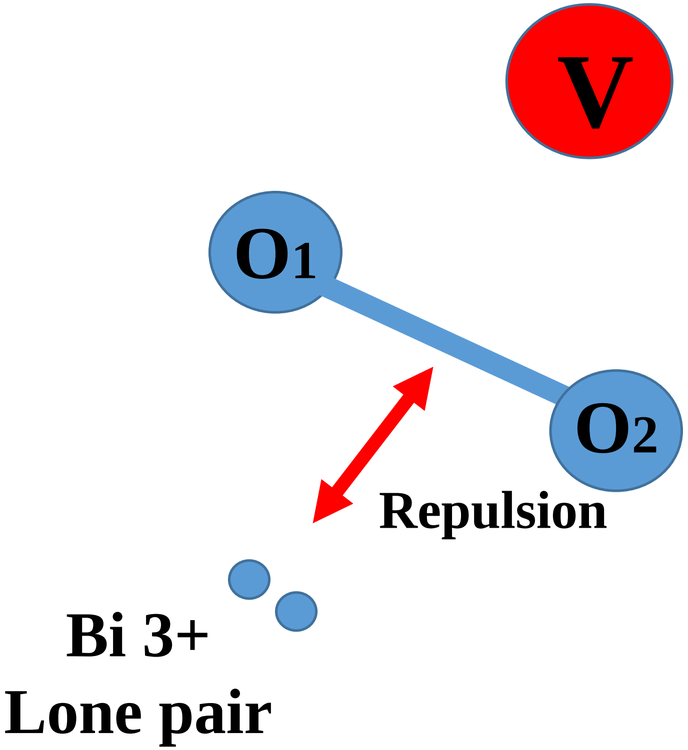
Table: Bond lengths obtained after refinement

Sample ID	Dodecahedral (A°)				Tetrahedral (A°)		O1 – O2
	Bi – O1	Bi – O2	Bi – O1	Bi – O2	V – O1	V – O2	
Pure m - BVO	2.372	2.628	2.516	2.354	1.770	1.691	3.118
BVO S1	2.353	2.515	2.370	2.626	1.766	1.690	2.747
BVO S2	2.372	2.630	2.517	2.355	1.770	1.689	2.954
BVO S3	2.372	2.627	2.518	2.355	1.771	1.689	3.118
BVO S4	2.375	2.639	2.519	2.364	1.774	1.694	**3.743**

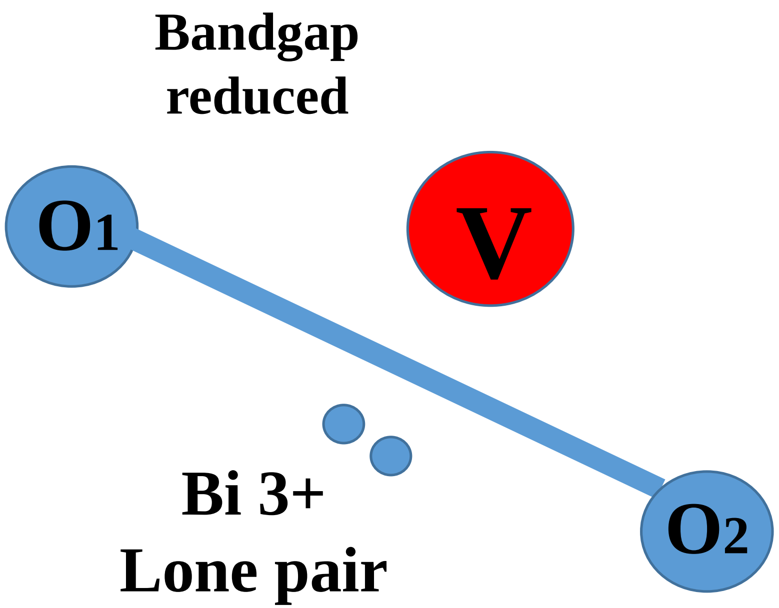
Results & Discussions

- Bond lengths of BVO S2 & BVO S3 match with the pure m – BVO
- Doping with 10% Nd **does not create any distortion** rather suppresses
- Doping at dodecahedral site is not effective due to its larger volume at its center than tetrahedral
- With the increase of %Nd doping, % tetragonal phase will increase and result a monoclinic – tetragonal zircon type heterostructured BVO
- Doping with 10% Mn, stretches O1 – O2 and the reason is strong Mn – O interaction
- Due to stretched O1 – O2, energy state of Bi^{3+} becomes **lower** than Oxygen p orbital & **desired distortion happened**

Results & Discussions



Without Mn doping



With Mn doping

Suggestions for Future Research

- ❖Photocatalytic experiment is recommended for Mn doped BVO
- ❖Synthesis & characterization of monoclinic – tetragonal zircon type BVO with increased % Nd doping (> 10%)
- ❖Synthesis & characterization of Mn doped BVO with different % doping of Mn

References

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[8] Sara Usai, Sergio Obregón, Ana Isabel Becerro, and Gerardo Colón Monoclinic−Tetragonal Heterostructured BiVO4 by Yttrium Doping with Improved Photocatalytic Activity The Journal of Physical Chemistry C · November 2013 117, 24479−24484

Thank You

Any Questions?