

# **Investigating the Role of Selenium Ion Concentration on Opto-electronic Properties of the $\text{Cu}_2\text{ZnSn}(\text{S}_{1-x}\text{Se}_x)_4$ Thin Films**

Satish S. Patil<sup>1</sup>, Kishorkumar V. Khot<sup>1</sup>, Sawanta S. Mali<sup>2</sup>, Chang K. Hong<sup>2</sup>

Popatrao N. Bhosale<sup>1\*</sup>

Satish S. Patil<sup>1</sup>, Kishorkumar V. Khot<sup>1,2</sup>, Sawanta S. Mali<sup>3</sup>, Chang K. Hong<sup>3</sup>, Popatrao N. Bhosale<sup>1\*</sup>

<sup>1</sup>Materials Research Laboratory, Department of Chemistry, Shivaji University, Kolhapur,

416004, MS India

<sup>2</sup>School of Nanoscience & Technology, Shivaji University Kolhapur, 416004, MS India

<sup>2</sup>School of Applied Chemical Engineering, Chonnam National University, Gwangju, South Korea.

Corresponding Author Email: [p\\_n\\_bhosale@rediffmail.com](mailto:p_n_bhosale@rediffmail.com)

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**Table S1:** Comparative XRD data of the CZTSSe thin films

A comparative experimental and standard ‘d’ values of the CZTSSe films were determined using relation,  $\Delta d(\text{\AA}) = d_{\text{exp}}(\text{\AA}) - d_{\text{JCPDS}}(\text{\AA})$

Sr. No.	JCPDS Data	$2\theta$ (Degree)	( $hkl$ )	$d_{\text{Exp}}$ (\text{\AA})	$d_{\text{JCPDS}}$ (\text{\AA})	$\Delta d(\text{\AA}) =$ $d_{\text{Exp}}(\text{\AA}) - d_{\text{JCPDS}}(\text{\AA})$
1		28.76	112	3.324	3.234	0.09
2	<i>Cu<sub>2</sub>ZnSn(SSe)<sub>4</sub></i>	47.30	220	1.932	1.849	0.09
3	(26-0575)	56.43	312	1.698	1.646	0.05
4		60.99	224	1.576	1.545	0.03

**Table S2:** Compositional analysis parameters of the deposited CZTSSe thin films

The observed Zn/Sn, Cu/(Zn+Sn) and (S+Se)/(Cu+Zn+Sn) stoichiometric ratio and atomic percentage of elements for CZTSSe thin film as function of Se<sup>2-</sup> ion concentration.

Sample Code	Cu	Zn	Sn	S	Se	$\frac{\text{Zn}}{\text{Sn}}$	$\frac{\text{Cu}}{(\text{Zn} + \text{Sn})}$	$\frac{(\text{S} + \text{Se})}{(\text{Cu} + \text{Zn} + \text{Sn})}$
<b>Se<sub>1</sub></b>	24.8	13.3	12.5	49.4	0.0	1.06	1.01	0.97
<b>Se<sub>2</sub></b>	23.8	12.4	12.8	40.8	10.2	0.96	0.95	1.04
<b>Se<sub>3</sub></b>	25.2	10.8	13.7	34.6	15.7	0.78	1.02	1.01
<b>Se<sub>4</sub></b>	23.6	12.5	11.2	30.9	21.8	1.11	0.99	1.11
<b>Se<sub>5</sub></b>	22.4	12.2	11.8	27.2	26.4	1.03	0.93	1.15

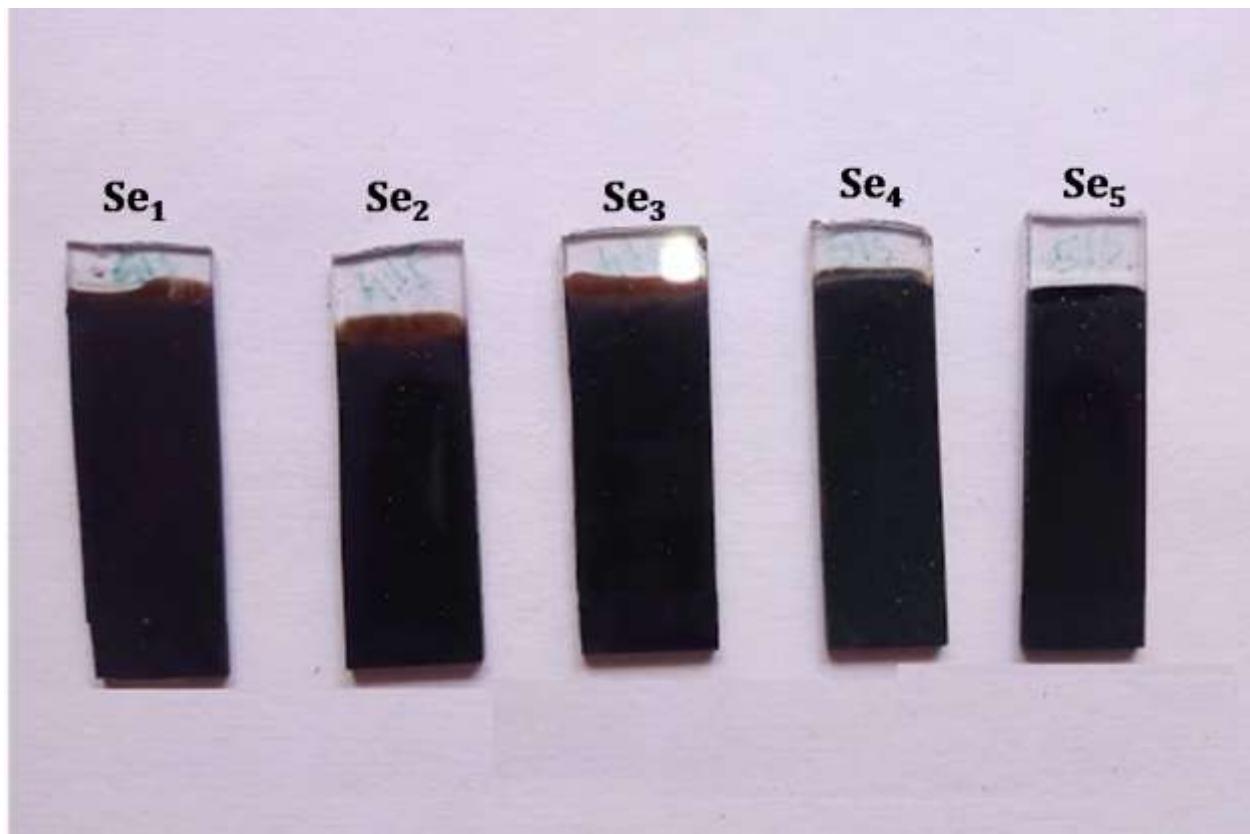
**Table S3:** EIS parameters of the CZTSSe thin films

Values of series resistance (Rs), charge transfer resistance (Rct), double layer capacitance (Cdl), Warburg impedance and Bode phase angle for CZTSSe thin film

<b>Sample Code</b>	<b>Rs (<math>\Omega/\text{cm}^2</math>)</b>	<b>Rct (<math>\Omega/\text{cm}^2</math>)</b>	<b>Cdl (<math>\text{F}/\text{cm}^2</math>)</b>	<b>Zw (mMho)</b>	<b>Bode phase angle</b>
<b>Se<sub>1</sub></b>	32.4	465	6.53	1.76	-57.2°
<b>Se<sub>2</sub></b>	32.6	203	7.57	10.9	-54.2°
<b>Se<sub>3</sub></b>	26.4	124	10.5	4.26	-25.6°
<b>Se<sub>4</sub></b>	67.9	40.4	6.19	10.9	-8.2°
<b>Se<sub>5</sub></b>	73.7	68	107	21.4	-20.1°

**Figure S1.** Photographs of the deposited  $\text{Cu}_2\text{ZnSn}(\text{S}_{1-x}\text{Se}_x)_4$  ( $x=0.0$  to  $0.1$  M Se) thin film

Lab scale physical photographs of hydrothermally deposited  $\text{Cu}_2\text{ZnSn}(\text{S}_{1-x}\text{Se}_x)_4$  thin film with varying  $\text{Se}^{2-}$  ion concentration



**Figure S2:** Thickness measurement of deposited  $\text{Cu}_2\text{ZnSn}(\text{S}_{1-x}\text{Se}_x)_4$  films as a function of Se ion concentration

Thickness of deposited CZTSSe thin films were lies in the range of 425 to 545 nm with varying  $\text{Se}^{2-}$  ion concentration in  $\text{Cu}_2\text{ZnSn}(\text{S}_{1-x}\text{Se}_x)_4$  films. The increase in film thickness with  $\text{Se}^{2-}$  ion concentration in CZTSSe thin films up to  $x=0.075$  M and after that it slightly decreases.

