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# Thermopower Enhancement of Rutile-type SnO<sub>2</sub> Nanocrystalline Using Facile Co-Precipitation Method

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## Abstract

Metal oxide semiconductor has attracted so much attention due to its high carrier mobility. The thermoelectric study of nanocrystalline SnO<sub>2</sub> through a simple co-precipitation method is observed to enhance the Seebeck coefficient ( $S$ ). X-Ray Diffraction, Thermogravimetric Analysis (TGA), resistivity ( $\rho$ ), Seebeck coefficient ( $S$ ), and power factor (PF) measurements are conducted to analyze the thermoelectric properties of the material. The measurements show that there are two interesting results, which are the unusual resistivity behavior and the high value of the  $S$ . Resistivity behavior shows a non-reflective intermediate semiconductor-metals behavior where the turning point occurs at 250 °C. This behavior is strongly correlated to the surface oxide reaction due to annealing temperature. The maximum  $S$  likely occurs at 250 °C, since the curve shows a slight thermopower peak at 250 °C. The value of the  $S$  is quite high with around twenty times higher than other publications about SnO<sub>2</sub> thermoelectric material, this happens due to the bandgap broadening. The energy gap of SnO<sub>2</sub> calculated using Density Functional Theory (DFT) which was performed by Quantum Espresso 6.6, the result shows there is a broadening energy gap at different momentum or wave factor. Nanocrystalline semiconductors material is giving an impact to increase the width of bandgap due to quantum confinement and could enhance the thermopower especially in SnO<sub>2</sub> nanocrystalline.

**Keywords:** thermoelectric, Seebeck, co-precipitation, nanocrystalline, metal-oxide, tin-dioxide.

## I. INTRODUCTION

Thermoelectric materials are promising candidates as harvesting energy devices for converting waste heat into electricity [1]. Thermoelectric could be acting as solid-state refrigerators or heat pumps. One advantage of thermoelectric is it does not use any moving parts and environmentally harmful fluids. Due to their high reliability and simplicity, thermoelectric materials are used extensively in fields such as space power generation and a variety of cooling applications [2]. Thermoelectric performance is determined by the dimensionless figure of merit ( $ZT$ ) [2], [3], which is denoted by (1).

$$ZT = \frac{S^2 \sigma T}{\kappa} \quad (1)$$

where  $S$  is Seebeck coefficient representing a significant temperature difference which is required to generate electrical energy,  $\sigma$  is electrical conductivity,  $\kappa$  is thermal conductivity, and  $T$  is the absolute temperature. In order to increase thermoelectric material performance, elevating the optimization of the  $ZT$  value is required. To maximize  $ZT$  value, the  $S$ , large  $\sigma$ , and low  $\kappa$  are needed simultaneously. However, there are conflicting parameters in optimizing  $ZT$ , since the  $S$ ,  $\sigma$ , and  $\kappa$  are strongly coupled by carrier concentration ( $n$ ) and difficult to control those variables independently following Wiedemann-Franz Law [4], [5].

Based on equation 1, to achieve a high  $ZT$  value, the enhancement of the  $S$  is needed. There are two

conventional strategies to optimize the  $ZT$  values, which are: (1) enhancing the power factor (PF) by point defect engineering, and band engineering; (2) independently reducing the lattice thermal conductivity ( $\kappa_L$ ) by structural nano-crystallization, interface engineering, and hierarchical architect-ing, or designing novel thermoelectric materials with intrinsically low  $\kappa$  [6], [7].

A semiconductor material is a good candidate as a thermoelectric material since it can be doped to achieve single n-type or p-type carrier for enhancing the  $S$ . As mixed n-type and the p-type carrier will lead to lowering the  $S$  [8]. In other words, both low  $n$  and high  $n$  of semiconductor behavior can obtain the large  $S$ .

Several material types attracted so much attention in the thermoelectric application such as chalcogenide metals [9], SiGe alloy [10], [11], silicon based thermoelectric materials [12], and skutterudites [13]. There are several thermoelectric materials commercially provided from low to high temperature, which are Bi<sub>2</sub>Te<sub>3</sub> (300–500 K) [14], PbTe (500–600 K) [15], and SiGe (600– 800 K) [11]. The progress of thermoelectric material is still limited for practical application, since their applications are largely restricted by the toxicity, limited element resources, and material degradation at high temperatures because of the temperature limitation due to phase transformation at high temperatures [2], [16].

Metal oxide-based material is one of the candidates of thermoelectric application, since it has low-mobility materials properties, primarily because of its highly ionic characters, abundance in nature, and non-toxicity [16],

[17]. However, the lower  $\mu$  in metal oxide thermoelectric leads to larger lattice thermal conductivity and to achieve high ZT is quite difficult [5].

Tin-dioxide is one of the metal-oxide group that is a candidate of an n-type semiconductor material due to its electrical conductivity simultaneously with optical properties and high-temperature stability [18], [19]. SnO<sub>2</sub> has a wide-bandgap (3.6 eV) and the value of bandgap width is a fundamental property in semiconductor material [8], [20] to achieve desired properties such as elevating the  $S$  to enhance the ZT. Fonstad *et al.* reported the Hall mobility ( $\mu_h$ ) value of SnO<sub>2</sub> single-crystal was one-order larger than the drift mobility ( $\mu_d$ ) of copper [21].

SnO<sub>2</sub> as thermoelectric material has been synthesized using several techniques and showed a nearly similar  $S$  coefficient value. Ferreira *et al.* did SnO<sub>2</sub> n-type thermoelectric thin-film synthesis by radio frequency (rf) sputtering and showed  $S$  of -225  $\mu$ V/K,  $\rho$  below  $10^{-3}$   $\Omega$ .m, and around  $10^{-4}$  W/m.K<sup>2</sup> for PF [22]. Bagheri *et al.* also did SnO<sub>2</sub> thin films synthesis using spray pyrolysis technique and showed n-type thermoelectric. The  $S$  effect showed -255  $\mu$ V/K with n-type thermoelectric material and resistivity  $1.3 \times 10^{-2}$   $\Omega$ .cm [23]. SnO<sub>2</sub> has been synthesized using a solid-state method by Paulson *et al.* [18]. The results showed the  $S$  was between -220 and -230  $\mu$ V/K, crystallite size was 83.6 nm, and the PF was between 6 and  $7 \times 10^{-6}$  W/m.K<sup>2</sup>. However, the PF of each result showed big different values due to the  $\sigma$  for each material could be different due the size of the bandgap. The limiting point of SnO<sub>2</sub> as a thermoelectric application was low thermoelectric performance due to large thermal conductivity around 40 Wm<sup>-1</sup>K<sup>-1</sup>. Kerrami *et al.* published a modulation about enhanced ZT of SnO<sub>2</sub> by modulating the energy band structure through an applied strain [19].

In order to enhance the  $S$  coefficient, nanostructured materials are required. Nanostructured material often shows different properties with the bulk material due to strong surface interactions between closely packed nanoparticles, a large surface to volume ratio and quantum confinement effects due to the tiny size. Decreasing particle size will reduce the  $\kappa$  and preserve  $n$  due to confining electron motion into a specified energy level. The electron motion confinement makes discreteness of level energy and widens up the bandgap. Increasing the bandgap width generating enhancement of the  $S$  and could elevate the effectiveness of PF of the thermoelectric material [8], [20], [24].

This paper aims to characterize thermoelectric properties of undoped SnO<sub>2</sub> nanocrystalline. The co-precipitation method is used as a synthesis method to obtain nanocrystalline materials to increase the bandgap width to enhancing the  $S$ . This method used since the published papers about the synthesis SnO<sub>2</sub> co-precipitation method are rare to find because of the majority used for gas sensing and photovoltaic application. The method is commonly used to synthesized nanocrystalline materials [25]. Moreover, the co-precipitation method is facile, low energy, and practicable in reproducibility.

## II. EXPERIMENTAL SECTION

### A. Materials

SnCl<sub>2</sub>.2H<sub>2</sub>O (Merck) and Ammonia (Merck) were used as starting materials with 0.22 M and 2 M respectively using DI water as a solution to synthesize SnO<sub>2</sub> powder using a simple co-precipitation method. A magnetic stirrer with a hot plate was equipped to dissolve the SnCl<sub>2</sub>.2H<sub>2</sub>O in DI water at low-speed stirring under ambient temperature. The temperature of the solution increased to 40 °C while the ammonia slowly dropped into the solution until the pH reached 10 -11. Then the temperature was raised to 90 °C and the solution was stirred for 2 h.

The solution was let cool down to room temperature, then the precipitation was collected and cleaned for several times using DI water. The white powder was dried at 60 °C for 24 h and annealed at 800 °C for 2 h under ambient pressure.

### B. Characterization

The phase of powder SnO<sub>2</sub> was determined by using Bruker D8-Advance X-ray powder diffractometer with 0.02 angle steps between 20° to 90° of 2 $\theta$  using Cu K $\alpha$  radiation. The results were then refined using Rietveld analysis to obtain the lattice and structure parameter. The crystallite size and strain were calculated manually in python from the XRD pattern perspective using the Williamson-Hall (W-H) plot method [26], [27]. Grain size, morphology, and elemental composition of SnO<sub>2</sub> were determined using a Scanning Electronic Microscopy with an Energy Dispersive X-ray Microscopy (SEM/EDS) JEOL-JSM IT 300.

Thermoelectric properties of SnO<sub>2</sub> were examined using Linseis LSR-4 in the range of 150 to 450 °C of temperature. That range was obtained from Thermogravimetry Analysis (TGA) characterization using NETZSCH TG 209 F1 Libra TGA209F1E-00 with the heat rate 10°/min in the range 30 - 600 °C under an oxygen atmosphere. Band structure of SnO<sub>2</sub> nanocrystalline was analyzed using theoretical calculation using Density Functional Theory (DFT) method and performed by Quantum Espresso 6.6.

## III. RESULTS AND DISCUSSIONS

X-ray powder diffraction pattern of SnO<sub>2</sub> is shown in Figure 1, where all the peaks belong to SnO<sub>2</sub> structure with space group P 42/m n m and there is no peak belonging to other elements indexed to the Powder Diffraction File (PDF) cassiterite tetragonal SnO<sub>2</sub> (PDF-96-900-7434) [28]. The refinement was done using the Rietveld method [29] and obtained 1.6, 2.46, 8.61, and 5.49 for the Goodness of Fitting (GoF) index;  $\chi^2$ , Rwp, and Rf, respectively.

The crystallography structure is shown in Figure 2. The Sn-atom is surrounded by six oxygens and resulting rutile properties which have a tetragonal crystal structure. All refined parameters were shown in Table 1.

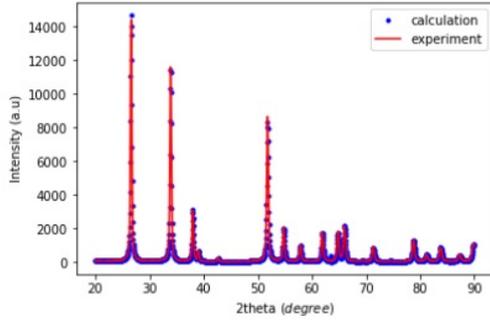


Figure 1. X-ray diffraction refinement.

TABLE 1. CRYSTAL DATA AND REFINEMENT RESULT FROM  $\text{SnO}_2$

Structure Parameter					
Atom	X	y	z	Uc	Site
Sn	0.00000	0.00000	0.00000	1.000	2a
O	0.30350	0.30350	0.00000	1.043	4f
Lattice Parameter					
a	B	c	$\alpha$	B	$\gamma$
4.7377 Å	4.7377 Å	3.1864 Å	90°	90°	90°

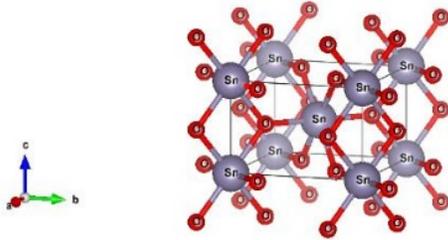


Figure 2. Structure of rutile  $\text{SnO}_2$ .

The peak broadening from X-Ray powder diffraction is a contribution from crystallite size and microstrain which represents the displacement of atoms from their original positions and instrumental broadening. Indirect crystallite size and microstrain determination could be done using the XRD pattern perspective [29] at least the Williamson-Hall (W-H) plot is used since the Scherrer equation gives a rough estimation of a crystallite size where the line broadening is only from crystallite size contribution and neglecting other parameters i.e. strain, instrumental broadening, preferred orientation, and shape factor. The smaller size of crystallite is causing the crystal growth limitation and change to imperfect crystal, which leads to broadening in the diffraction peak [26]. Williamson-Hall (W-H) plot is a technique to separate the contributions of crystallite size and microstrain to the peak broadening in X-Ray powder diffraction patterns with Lorentzian profiles which is denoted by (2) [27].

$$\beta = \beta_D + \beta_\epsilon \quad (2)$$

Scherrer equation is described in (3).

$$\beta_D = \frac{k\lambda}{D \cos\theta} \quad (3)$$

where  $\beta_D$  is Full Width Half at Maximum (FWHM) in radians [28],  $k$  is the shape factor,  $D$  is the crystallite size,  $\theta$  is the peak position in radians, and  $\lambda$  is the wavelength of the X-ray source.

Peak broadening contribution from micro-strain is given by (4).

$$\beta_\epsilon = 4\epsilon \tan\theta \quad (4)$$

where  $\beta_\epsilon$  is the FWHM due to strain and  $\epsilon$  is the strain. The Williamson-Hall equation can be written as (5).

$$\beta \cos\theta = \epsilon(4 \sin\theta) + \frac{k\lambda}{D} \quad (5)$$

Compared to the linear fitting equation, micro-strain value and crystallite size were obtained from the slope and intercept, respectively. The result is shown in Figure 3. The slope was obtained as micro-strain in negative value indicates that there is lattice compression [30] with -0.00033 occurrence. Then, the crystallite size from the W-H plot is around 70 nm.

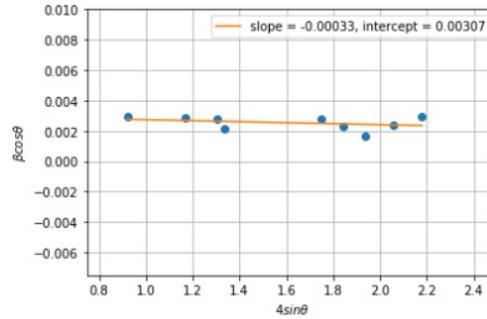
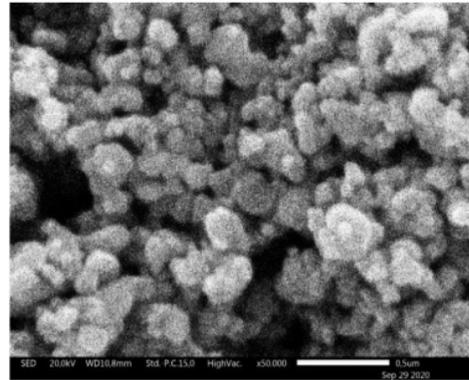


Figure 3. Williamson-Hall plot from  $\text{SnO}_2$ .

The morphology of  $\text{SnO}_2$  was scanned by SEM and the result in Figure 4(a) shows that the material most likely has a near-spherical shape that tends to oval shape. Other publication about co-precipitation  $\text{SnO}_2$  synthesis method showed a similar shape [31]–[33].



(a)

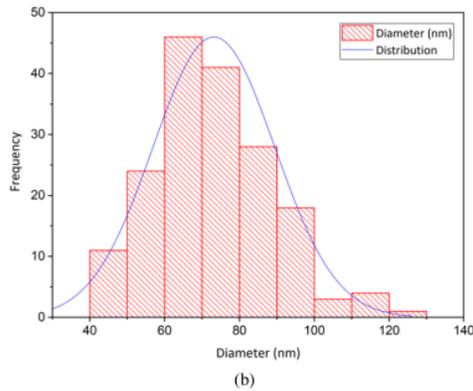


Figure 4. (a). SEM image of SnO<sub>2</sub> nanocrystalline. (b). Histogram and distribution curve of SnO<sub>2</sub> nanocrystalline shows frequency vs diameter of grain size (nm).

TABLE 2. WILLIAMSON-HALL PLOT DATA RESULT.

Sample	Strain	Crystallite Size (nm)	Grain Size from SEM (nm)
SnO <sub>2</sub>	-0.00033	70	71.1

The micrograph result obtains a distribution curve which resulted that the grain size is around 6 nm and shows in Figure 4(b). SEM measurement is a proper method to compare the crystallite size to the W-H plot with the real morphology of SnO<sub>2</sub> material approximation. Both methods give almost similar value. The results from the W-H plot method and SEM examination are summarized in Table 2.

The temperature range of SnO<sub>2</sub> thermoelectric properties is determined by TGA measurement to observe the decomposition of the sample then disappeared sample while thermoelectric measurement conducted could be avoided. Figure 5(a) shows the TGA result and its differential curve in figure 5(b).

TABLE 3. MASS CHANGE PERCENT FROM TGA MEASUREMENT RESULT

Mass Change (%)	Temperature Range (°C)	
	Min	Max
-0.32	26.4	112.7
0.18	112.7	286.0
-0.07	286.0	362.5
-0.76	362.5	599.9

The sample decreasing at 36.1 °C possibly represents the evaporation of some solvents. The changing mass of the sample occurs at four temperature ranges as shown in Table 3. Overall, the curve shows the sample undergoes multistage decomposition progress, however, there is an uncommon increasing weight at 113.2 - 286.3 °C due to oxidation [34] with gaseous substance since the measurement was conducted under oxygen atmosphere [29],[30]. In post-metal oxide material, when temperature increases, the material attracts an electron from oxygen which leads to increased weight due to surface oxide reaction. Then the weight losses of SnO<sub>2</sub> slowly decreased after 600 °C [36].

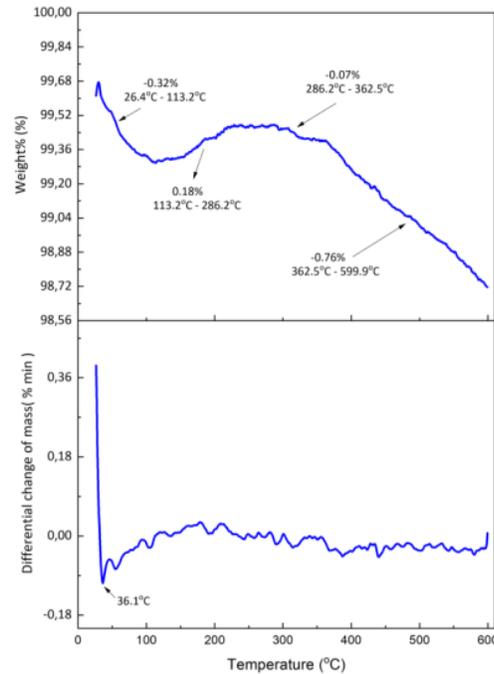
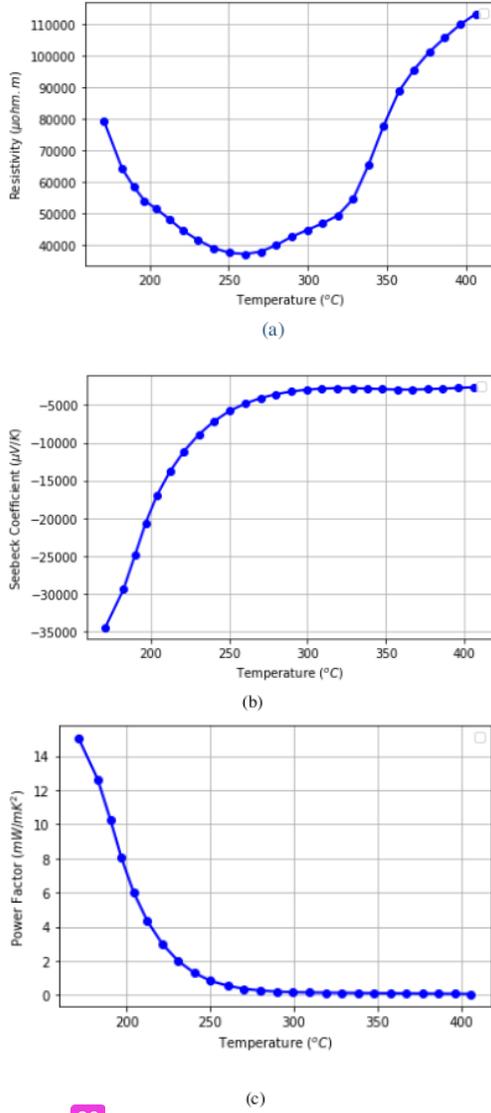


Figure 5. (a) TGA diagram of SnO<sub>2</sub> nanocrystalline and (b) Differential curve from TGA diagram of SnO<sub>2</sub> nanocrystalline.

The electrical resistivity curve in Figure 6(a) shows two-phase of the character of conductivity behavior. As the temperature increases, charge carriers are thermally activated which increases their drift mobility ( $\mu_d$ ) and decreases  $\rho$  from 150–260 °C, this shows a typical semiconductor, then the  $\rho$  starting to increase from 250 °C indicates metal conductivity characteristic. From the curve, it could be said that the character of SnO<sub>2</sub> conductivity exhibits non-reflective intermediate properties between semiconductor and metal.

This notable change could be strongly related to the TGA curve which has a slight increase in weight percentage around 113.2 - 286.3 °C, while temperature increases after 113.2 - 286.3 °C range, the oxygen seems to be excited at a higher temperature and the SnO<sub>2</sub> tends to have metal resistivity behavior. These properties are also found in CuO<sub>2</sub> [37] due to annealing temperature and the material phases formed are calculated using Lichtenecker's formula for resistivity of two-phase alloys.

The  $S$  curve is shown in Figure 6(b), the negative sign indicates that SnO<sub>2</sub> nanocrystalline is an n-type semiconductor. At a glance, the  $S$  is ten times higher than any other publication about SnO<sub>2</sub>. This is caused by the  $S$  in semiconductor will be much larger than it is in metals due to the presence of a bandgap which breaks the symmetry between electron and hole [38]. The  $S$  curve did not show a clear thermopower peak, but the point at 250 °C is noteworthy which shows  $-5.79 \times 10^3 \mu\text{V/K}$ .



26 Figure 6. Thermoelectric properties result (a) Resistivity (b) Absolute seebeck coefficient, and (c) Power factor.

The absolute  $S$  at temperature ( $T$ )  $< 250$  °C drops significantly followed by conductivity as [12], this is typically semiconductor behavior since the Fermi level is moving into the valence band [38]. The  $S$  at  $T > 250$  °C, the curve decreases slowly and shows metals behavior due to increasing conductivity.

The relation [16] between the energy gap and the  $S$  in a semiconductor. Goldsmid and Sharp developed an analytical expression on the bandgap and the maximum Seebeck coefficient through Goldsmid-Sharp in (6) [24], [39].

$$E_g = 2e|S|_{max}T_{max} \quad (6)$$

25 where  $E_g$  is the energy gap,  $|S|_{max}$  is Seebeck coefficient maximum, and  $T_{max}$  is the temperature where the  $S$  maximum occurs. Goldsmid-Sharp is a useful tool for estimating the energy gap through temperature dependence  $S$  measurement value [24].

Theoretical computation of band structure is employed as an explanation about the bro[12]ning band gap which occurs in SnO<sub>2</sub> nanocrystalline using Density Functional Theory (DFT). The gap energy of material has different values for each wave factor or momentum, hence, all the Brillouin Zone (BZ) should be included in reciprocal space. To determine the energy gap and correct the charge-charge and spin-spin interaction, an exchange-correlation function is needed. There are a lot of exchange-correlation function types and the property is unique for each m[24]al structure.

In this paper, a band structure and Density of S[23] (DOS) were performed using Quantum Espresso 6.6 [40] with Projector Augmented Wave (PAW) [41] and PBEsol exchange-correlation which is generally used to determine the energy gap [42]. Band structure and DOS are calculated using lattice constant from the experiment result and compared with the optimized structure to represent the bulk structure ( $a = 4.7690$ ,  $c = 3.2295$ ).

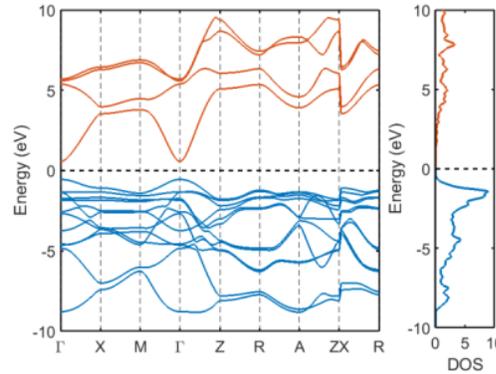


Figure 7. Band structure and DOS of SnO<sub>2</sub> nanocrystalline calculation using DFT.

The PBEsol exchange-correlation method is used to explain the gap energy broadening phenomena, however, to obtain the gap energy near to the exact value needs another exchange-correlation method which is more complex than PBEsol [43]. In this paper, the use of the PBEsol exchange-correlation method is proper enough to explain the broadening c[32]he energy gap phenomena. The calculation result is shown in Figure 7, the energy gap minimum at  $\Gamma$  position has 1.114 eV from the experiment structure and 0.781 eV from the optimized structure and all energy gap calculation results at each position are summarized in Table 4.

TABLE 4. ENERGY GAP RESULT FOR EACH POSITION.

Position	Energy Gap (eV)	
	SnO <sub>2</sub> Optimized Structure	SnO <sub>2</sub> nanocrystalline
$\Gamma$	0.781	1.11
X	4.310	4.614
M	4.852	5.204
Z	6.504	6.866

R	6.273	6.581
A	4.921	5.233

It is clearly seen that the SnO<sub>2</sub> nanocrystalline shows a broadening of the energy gap at each position. This result is in good agreement with Zhou et. al. publication which exhibits a similar result with this paper for energy gap broadening compared to the optimized structure and the experiment structure at  $\Gamma$  position [44]. The broadening value of the energy gap from the experiment at  $\Gamma$  position occurs due to lattice compression [44] which is shown in Table 5. The lattice compression is also exhibited in the W-H plot calculation and shows a negative strain value due to decreasing crystalline size [30], [45].

TABLE 5. LATTICE PARAMETER COMPARISON BETWEEN OPTIMIZED STRUCTURE (BULK) AND NANOCRYSTALLINE STRUCTURE.

Lattice Parameter	SnO <sub>2</sub> Optimized Structure	SnO <sub>2</sub> nanocrystalline
a	4.7690 Å	4.7364 Å
b	4.7690 Å	4.7364 Å
c	3.2295 Å	3.1857 Å

Nanocrystalline on SnO<sub>2</sub> semiconductor is most likely give an impact to the increase in the width of the bandgap due to quantum confinement and the effect of the internal strain. The nano-structuring makes the particle too small to be comparable with the wavelength of the electron, the motion of the electron is restricted to the specified energy through quantum confinement.

The confinement of moving electrons is making the valence and conduction band split and discrete due to restricted the electron movement into specified energy, which results in widening up the bandgap [8], [20], [46]. Sahana et al [20] increased the SnO<sub>2</sub> bandgap from 3.89 to 4.5 eV through nano-structuring by a controlled choice of composition and annealing temperature. The enhancement of thermopower due to quantum confinement is also giving an impact on lowering the  $\kappa$  [8], [47].

Figure 6(c) shows SnO<sub>2</sub> reaches the maximum PF at 171 °C with the value of  $15.03 \times 10^{-2} \text{ W/m.K}^2$ . This value is much related to the  $S$  and  $\sigma$ . When the temperature is rising, the charge carrier conductivity also increases.

Nonetheless, the high  $S$  value cannot meet the clarity yet since many things could affect the materials. However, the strong one which is correlated to the enhancement of the  $S$  is the bandgap of the materials with temperature influences. Both resistivity behavior and the interesting  $S$  in SnO<sub>2</sub> nanocrystalline need further investigation using a comprehensive bandgap measurement and theoretical approach relating to the oxygen occupancy and the temperature influence to the bandgap modification.

## CONCLUSION

In summary, SnO<sub>2</sub> nanocrystalline was synthesized using the facile co-precipitation method. The thermoelectric properties were examined and showing two interesting results, which are the electrical resistivity ( $\rho$ ) behavior to the increasing temperature due to surface oxide reaction and the high Seebeck coefficient ( $S$ )

around twenty times higher than other publications. The relationship between the  $S$  and nano-structuring value is strongly correlated to the bandgap broadening due to the quantum confinement process. However, those arguments need further investigation by energy gap characterization and comprehensive theoretical approach.

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