New simple synthesis, crystal system and physical properties of Zn$_5$S$_2$ compound

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Abstract. We report a large-scale solid-state synthesis of non-stoichiometric Zn$_5$S$_2$ powders at considerably low (400 K) sintering temperatures. The DTA measurement has been carried out to reveal the temperature dependence phase transformation of the samples. Our best powder XRD refinement analysis so far shows that the studied compound belongs to monoclinic P2$_1$C with $a = 5.2538\, \text{Å}$, $b = 19.3137\, \text{Å}$, $c = 3.4543\, \text{Å}$, $\beta = 90.176^\circ$. The I-V measurement shows that our Zn$_5$S$_2$ samples to be potentially p-type semiconducting material. Thus, from our preliminary characterizations, we can conceive that these Zn$_5$S$_2$ could be potentially great p-type thermoelectric materials. The ongoing thermoelectric properties characterizations of these compounds are discussed in this contribution.

1. Introduction

Indonesia is the fifth most populous country in the world [1], the human population is proportional to energy demand [2]. Indonesia abounds with energy resources (steam coal, natural gas, oil). But, we face several challenges are increasing energy efficiency and using renewable energy. The gas sector should be further developed becomes renewable energy, especially geothermic [3]. Geothermic energy potential in Indonesia is estimated about 40% of the world geothermic energy potential. However, only approximately 4.5% is being utilized as energy. Another type of renewable-energy potentials such as hydro energy, wind energy, wave energy and biomass potential. But these sources depend on weather, climate and expensive [4].

Based on this reason, we need to increase quantity and quality of renewable energy. The thermoelectric generator is one of renewable energy alternative [5]. Thermoelectric can generate electric energy from thermal energy and vice versa. Therefore thermoelectric materials are crucial in renewable energy conversion technologies to solve the global energy crisis [6]. Recent studies about thermoelectric are Tellurium based, but Tellurium is rare, and toxic [7]. So, we need to synthesis non-Tellurium compound. We choice sulfide compound because of one of the most widespread on Earth’s crust [8].

Thermoelectric technology is regarded as an alternative and environmentally friendly technology for harvesting and recovering heat which is directly converted into electrical energy [9]. In the case of
thermoelectric materials, the thermoelectric figure of merit (ZT) can be defined as follows: 
\[ ZT = \frac{\alpha^2 \sigma}{\kappa}, \]
where \( \alpha \) = Seebeck coefficient, \( \sigma \) = electric conductivity, \( \kappa \) = thermal conductivity, and \( \alpha^2 \sigma \) = power factor. For ideal thermoelectric materials, ZT should be 1 to obtain a conversion efficiency of > 10% [6]

2. Research Method
Zn\textsubscript{5}S\textsubscript{2} was prepared with high purity elements of Zinc (Zn) and Sulfur (S) as sources, which were weighed according to their respective stoichiometry. The reaction equation follows
\[ 5 \text{Zn}_{(s)} + 2 \text{S}_{(s)} \rightarrow \text{Zn}_5\text{S}_2_{(s)} \]

Based on this equation, to synthesize 7 grams of Zn\textsubscript{5}S\textsubscript{2}, we need 5.852 grams Zn and 1.148 gram S. We synthesized this compound using solid-state sintering. The design of synthesis is given in Figure 1. After being uniformly mixed, the mixture was pressed into a pellet. The sample was heated at 130 °C for 14 hours, 140 °C for 19 hours and 38 hours. On heated process, we covered the sample by carbon active to pretend oxidation. The design of procedure of Zn\textsubscript{5}S\textsubscript{2} synthesis is described in Figure 1. The scheme of sample structure during sintering process is illustrated in Figure 2.

| Zinc          | Sulfur          |
|---------------|-----------------|
| Mixed and ground to obtain fine and homogen powder |
| Pressed into pellet |
| Sintered at 130°C for 14 hours |
| Reground |
| Pressed into pellet |
| Sintered at 140°C for 19 hours |
| Reground |
| Pressed into pellet |
| Sintered at 140°C for 38 hours |
We used Energy Dispersive X-Ray Spectrometer (EDX) to obtain the elemental composition, Differential Thermal Analysis (DTA) and Thermogravimetric (TGA) for thermal analysis, X-Ray Diffractometer (XRD) to analysis structure. We further measure electrical conductivity using I–V meter and characterize band gap using Ultraviolet-Visible Spectrometer (UV Vis). We further analyze X-RD pattern to search the possible crystal system using DICVOL under Fullprof software.

3. Results and Discussion

3.1 Composition Analysis

The composition analysis of this compound was measured by Energy Dispersive X-ray spectroscopy (EDX). The result of EDX is given in Table 1.

| Compound | Composition (%) |
|----------|-----------------|
| Zn       | 49.98           |
| S        | 19.51           |

Our analysis shows that the studied compound belongs to Zn₅S₂. This compound was suitable for the purpose of this research.

3.2 Thermal Analysis

The thermal analysis was investigated by Differential Thermal Analysis (DTA). There are two results of DTA measurement. First, measurement on 140°C with increment 1°C, the peak was found on 116°C. Second, measurement on 600°C with 5°C increment, the peaks were found on 119.21°C and 422.49°C. Both of these results are explained in Figure 3 and Figure 4. Based on Figure 3, the peak of 116°C is endotherm.
Figure 3. Graph of DTA Zn$_5$S$_2$ on 140°C with an increment of 1°C

Figure 4. Graph of DTA Zn$_5$S$_2$ on 600°C with an increment of 5°C

Figure 4 shows two measurements, i.e., Differential Thermal Analysis (DTA) and Thermogravimetric (TGA) measurements. The peak at 119.21 °C is showing exothermic, while the existing peak at 422.49 °C is indicating an endothermic. TGA is the measurement of the mass of a sample as the temperature increase. The result shows that the mass of Zn$_5$S$_2$ loss as the temperature increases because the reactant became product and gas.

3.3 Structure Analysis
The structures were investigated by X-Ray Diffraction (XRD). The structure pattern of this compound is given in Figure 5.

Figure 5. XRD patterns of Zn$_5$S$_2$
We have compared the observed pattern with the only ZnS sphalerite in the database. By observing the pattern, it should be a single phase and ZnS sphalerite phase. We then further analyzed this compound using DICVOL optimized under Fullprof program. By inputting the xy data from X-Ray Diffraction pattern, we firstly plot this data using winPLOTR. Then we select peaks by using automatic peak search button on point selection section. We choose all crystal system and press Run DICVOL button on the External application. We found several structures from this analysis which is displayed in Table 2.

| System crystal | a (Å)   | b (Å)   | c (Å)   | Volume (Å³) | Figure of merit M | F |
|----------------|---------|---------|---------|-------------|-------------------|---|
| Tetragonal     | 13.9918 | 13.9918 | 78.2780 | 153.45      | 18.3              | 9.1  |
| Orthorombic    | 15.4670 | 52.1114 | 49.5693 | 399.53      | 13.4              | 6.6  |
| Monoclinic     | 5.2538  | 19.3137 | 3.4543  | 350.50      | 10.2              | 4.7  |

We choose the lattice parameter, structure of this compound by the smallest error value, belongs to P2₁/m a = 5.2538 Å, b = 19.3137 Å, c = 3.4543 Å, β = 90.176 o, volume= 350.50 Å³, figure of merit M = 10.2 and F = 4.7. The volume of Zn₅S₂ crystal 2 times greater than volume of ZnS crystal from database of standard ZnS sphalerite.

3.4 Electrical conductivity
The electric conductivity of Zn₅S₂ was measured by 2 probe I-V meter. The measurement was repeated 75 times. The graph voltage and current Zn₅S₂ explained in Figure 6. The result of electric conductivity is $5.95 \times 10^{-9} (\Omega^{-1} \text{m}^{-1})$. The positive σ values imply a p-type conducting behaviour [7].

![Figure 6. Graph of voltage and current Zn₅S₂ by I-V meter 2 probe measurement](image-url)
3.5 Bandgap analysis

In a solid material, electrons exist at energy levels that combine to form energy bands. The region between the valence band and the conduction band is called the forbidden band, where no electrons exist. For a conductor, no forbidden band exists. For an insulator, this band is so broad that the electrons require high energy to move from the valence band to the conduction band. For semiconductors, the gap of the forbidden band is smaller than for an insulator [10].

The band gap of Zn$_5$S$_2$ was analyzed using absorbance of Ultraviolet-visible spectroscopy (UV Vis) characterization. The data is depicted in Figure 7. The calculation of band gap energy was using Tauc Plot method given in Figure 8. The result of band gap energy analysis is $5.98 \times 10^{-19} \text{J} = 3.7 \text{eV}$; this result has a suitable value of ZnS band gap energy because ZnS has wide energy band semiconductor with a range of 3.6 – 3.9 eV. [11].

![Figure 7. Graph of wavelength and absorption Zn$_5$S$_2$ by UV Vis measurement](image1)

![Figure 8. Graph of energy and absorption calculation Zn$_5$S$_2$ by Tauc Plot Method](image2)
4. Conclusion
The new compound Zn$_5$S$_2$ has been successfully synthesized by using a simple method solid state sintering utilizing sandwiched carbon active. The most possible crystal system of this compound fall to monoclinic under space group of P2$_1$/m, with lattice parameters of $a = 5.2538\, \text{Å}$, $b = 19.3137\, \text{Å}$, $c = 3.4543\, \text{Å}$, $\beta = 90.176^\circ$. The thermal analysis we found that there were two phases, exothermic on peak 119.21 °C and endotherm on 422.49 °C. The electric conductivity of this compound is $5.95 \times 10^{-4} \, \Omega^{-1} \, \text{m}^{-1}$). The positive $\sigma$ values imply a p-type conducting behavior. The energy band gap about 3.7 eV and has sa suitable value for sa emiconductor. So, we conclude that Zn$_5$S$_2$ compound has potential become thermoelectric or supercapacitor materials.

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