The effect of Ag on thermoelectric performance of Cu$_{1-x}$Ag$_x$S tetrahedrite/Al prepared using modified polyol methods

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Abstract. In principle, thermoelectric technology is a semiconductor which capability to convert thermal energy into electrical energy. We used Ag-doped CuS deposited on aluminum foil as a sample understudied. The Cu$_{1-x}$Ag$_x$S was prepared using a modified polyol method. Firstly, CuS powder was dissolved together with dopant using TEG (TetraEthylene Glycol) and NaBH$_4$ with nitrogen, heated at 200 °C, and followed by centrifuged at 5000 rpm. The Characterization of CuS was carried out using XRD, SEM, and I-V. It is shown that the electrical conductivity tends to increase with increasing the Ag dopant. The highest electrical conductivity was reached at 70 °C. We also found that the crystallinity enhanced with the addition of Ag into CuS. Meanwhile, morphological inspection revealed that the increase of Ag, causing changes in grain shape.

Keywords: CuS, Ag, polyol, tetrahedrite

1. Introduction
The use of electric energy in Indonesia continues to increase along with the increase in population and various demands. Energy harvesting is one of the solutions to meet electricity demand in Indonesia. Meanwhile, harvesting energy utilization in Indonesia has not been maximized. One of the energy harvestings that can be used as an electric energy generator in Indonesia is thermoelectric. Thermoelectric is a device that can convert heat energy into electrical energy [1]. This technology, in principle, is a technology that uses a thermal energy-driven material and converts it into electrical energy [2]. This thermoelectric works when in the edges of the materials have different temperatures [3].

This study uses CuS material [4], which has several advantages, such as its short dissolution of the synthesis process [5], easily available support materials, simple procedures, and low cost. Several works have reported the use of polyol method in the synthesis of CuS based materials. The polyol method also uses nitrogen gas, which can reduce the content of the oxide in the sample, which aims to reduce the corrosion properties in the sample [6]. In the modification of the polyol method, additional solvent and reductor of TEG and NaBH$_4$ were implemented. There are several reports related to undoped CuS thermoelectric materials [7]. Ag as doping is one of the transition metals in class IB,
which is often used as doping. The dopant is easily available in nature. It is expected that certain concentrations of Ag in CuS enhance thermal conductivity lower than its electrical conductivity. Therefore, Ag acetate as doping in a thermoelectric is expected to affect many factors such as microstructure, thermal conductivity, bandgap, and electrical conductivity[8].

2. Research Method

2.1. CuS Synthesis
Copper (II) monohydrate acetate, sulfur, and silver acetate (≥98%, Aldrich) were dissolved in 100 mL of tetraethylene glycol (99%, Aldrich) in a 100 mL beaker glass. Followed by stirred on the magnetic stirrer under the flow of nitrogen gas for ± 10 minutes. Furthermore, sodium borohydride (4 g, 100 mmol) was dissolved in 100 mL of tetra ethylene glycol were sonicated and mixed in the base solution to produce a black solution which was then heated at 150 ºC under the flow of nitrogen gas for 1 hour. The mixture was cooled to room temperature. The cold mixture was put into 50 mL centrifuge tubes and centrifuged at 5000 rpm for ± 10 minutes. The procedure was repeated for different silver dopant of 0; 0.03; 0.05; 0.08; 0.1 mol to obtain Cu$_{1-x}$Ag$_x$S tetrahedrite materials.

2.2. Preparation of Thin Layers
The obtained powders from the previous modified polyol method were then dissolved in DMF (Dimethylformamide). On the other hand, we also prepared a clean aluminum foil using alcohol as the substrates. The formed solution deposited on the aluminum foil substrate using a doctor blade.

2.3. Characterization
The phase analysis was carried out using XRD (Pan Analytical type XPERT-PRO). The morphological and elemental characterization were carried out using SEM (FEI, Type: Inspect-S50). The electrical properties were obtained from the 2-probe method with the distance between the probes being 1 cm at various temperatures.

3. Results and Discussion
Figure 1 shows a single phase of CuS diffraction pattern, which associates to COD 9008368. The CuS crystal fits to a hexagonal system with a space group of P63/mmc which has $a = b = 3.796\text{Å}$, $c = 16.382\text{Å}$ and $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$. The highest peak in the histogram expresses diffraction from (110) of CuS at a diffraction angle of 48.016° [4]. Peak intensity appears at 2θ positions of 27.22°, 27.70°, 29.29°, 32.78°, 48.02°, 52.78°, and 59.29° are associated to (010), (012), (006), (008), (110), (018), and (116) Bragg’s planes, respectively.
Figure 1. XRD patterns of CuS nanoparticles.

Figure 2. XRD pattern of Cu$_{1-x}$Ag$_x$S (a) nanoparticles, and the shift of (110) peak (b).

Figure 2a shows the XRD pattern of Cu$_{1-x}$Ag$_x$S with various x fraction of Ag. As the silver dopant substitutes into the Cu site, the (110) peak shifts to a lower diffraction angle. This shift is to follow the theoretical aspect. The ionic radius of Ag is higher than Cu. When a view amount of Cu substitutes in Cu sites, the lattice enhance and denoted by the shift of several peaks to a lower angle.
Table 1. Phase fraction and Crystallinity of Cu$_{1-x}$Ag$_x$S.

| Ag dopant (x) | Crystallinity (%) | Phase fraction (%) |
|---------------|-------------------|-------------------|
| 0             | 23.43             | 81.89             |
| 0.03          | 24.07             | 59.06             |
| 0.05          | 24.20             | 58.96             |
| 0.08          | 27.24             | 58.13             |
| 0.1           | 31.00             | 57.39             |

From the XRD patterns, the crystallinity and phases fraction were analyzed using the GSAS software. The phase fraction was calculated from the identified peaks divided by the total peaks. On the other hand, the crystallinity of the samples was calculated Equation 1 [9] from refined using the GSAS application and further analysis using spreadsheet software.

\[
\%\text{crystallinity} = \frac{\text{crystalline area}}{\text{crystalline area} + \text{amorphous area}} \times 100\% 
\]  

Further analysis of the undoped sample, we found that the average particle size falls to 17.73 nm. This size is smaller than the previous study [10].

The morphology of Cu$_{1-x}$Ag$_x$S films is shown in Figure 2. Each sample has a spherical and specific porous. The SEM images were examined using ImageJ to obtain the average grain size. The grain size of Cu$_{1-x}$Ag$_x$S is different for each sample. The detail of the average grain size is 94.15 nm, 81.91 nm, 64.99 nm, 54.81 nm, and 51.20 nm, stand for x of 0.00, 0.03, 0.05, 0.08, and 0.1, respectively. In other research also showed a spherical and irregular morphology due to the effect of microwave radiation during synthesis [11]. But in some cases of CuS sample has different shapes and shows a larger size. The higher the temperature used, it will produce a large size[12].

![Figure 3. The top-view SEM image of Cu$_{1-x}$Ag$_x$S film.](image-url)
Table 2. The elemental composition of Ag in Cu\text{\textsubscript{1-x}}Ag\text{\textsubscript{x}}S.

| Ag dopant, x (Ag) At\% |
|------------------------|
| 0.0                    | 00.00 |
| 0.03                   | 01.22 |
| 0.05                   | 02.85 |
| 0.08                   | 03.91 |
| 0.1                    | 07.95 |

Table 2 is the EDX report. The EDX result indicates that the silver dopant, which was prepared using modified polyol, is successfully incorporated into Cu\text{\textsubscript{1-x}}Ag\text{\textsubscript{x}}S compound nanoparticles. From that results, it can be seen that with the increasing stoichiometric fraction of Ag, the Ag atomic composition increases.

Figure 4. The electrical conductivity of Cu\text{\textsubscript{1-x}}Ag\text{\textsubscript{x}}S.

The electrical conductivity of Cu\text{\textsubscript{1-x}}Ag\text{\textsubscript{x}}S film was characterized using a 2-point probe method. Figure 4 shows the electrical conductivity of Cu\text{\textsubscript{1-x}}Ag\text{\textsubscript{x}}S film with various x fraction of Ag. The increase of Ag content increases the electrical conductivity of Cu\text{\textsubscript{1-x}}Ag\text{\textsubscript{x}}S film.

For a specific purpose of the thermoelectric application, we need the information about the thermal performance of electrical conductivity. Figure 5 shows the electrical conductivity at various temperatures (a) and its thermal stability (b) of Cu\text{\textsubscript{1-x}}Ag\text{\textsubscript{x}}S film. In general, the conductivity has an order of $10^{-4}$ to $10^{-5}$ S/cm, indicating the thin film is a semiconductor[13]. It is known that the electrical conductivity increases with the increasing temperature. The highest increase in conductivity was at 70 °C and then decreased after passing the temperature of 70 °C. The electrons in the conduction band of lower temperature are free to move. On the other hand, at higher temperatures, the electrons may agitate, and more interaction creates more resistance. [14]. At lower temperature, the number electrons cause the current to increase so that the electrical conductivity also increases [15].
4. Conclusion
The addition of doping Ag to CuS nanomaterials gives rise to an increase in the grain size and crystallinity. The addition of Ag into CuS nanomaterials causes changes in the shape of the grain from ovalish to spherical. Ag addition increases conductivity at low temperatures and low doping, while high temperatures show different tendencies. The increase of Ag in Cu$_{1-x}$Ag$_x$S may increase the electrical conductivity at all temperature range, while at a higher temperature may reduce the conductivity.

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