CHAPTER 3

RESULTS AND DISCUSSION

This research results was divided into 3 parts. First, simulation structure of $Cu_{0.5}Ag_{1.5}InSe_3$ was presented. Then, the conditions of gel preparation were studied. Finally, the results of physical properties and electrical properties of gel and powder were characterized. The obtained results were reported and discussed as follows.

3.1 Results of $Cu_{0.5}Ag_{1.5}InSe_3$ simulation.

$Cu_{0.5}Ag_{1.5}InSe_3$(CAIS) structure was simulated from CaRIne 3.1 program. Since $Cu_{0.5}Ag_{1.5}InSe_3$ structure is the new structure. There was no reference database; JCPDS. The structure consists of 4 elements with high atomic number. There were Copper (Cu), Silver (Ag), Indium (In) and Selenium (Se) and its atomic number were 63.55, 107.86, 114.82 and 78.96 respectively. Each atom of elements effected to vibration frequency of CAIS.

The X-ray diffraction patterns of $Cu_{0.5}Ag_{1.5}InSe_3$(CAIS) was obtained from the structure simulation and it was used to confirmed the structure of synthesis product.

The diffraction pattern of the simulated structure of $Cu_{0.5}Ag_{1.5}InSe_3$ was showed in Figure 3.1. In addition, 2θ (h k l) and intensity of peak of $Cu_{0.5}Ag_{1.5}InSe_3$ was shown in table 3.1.

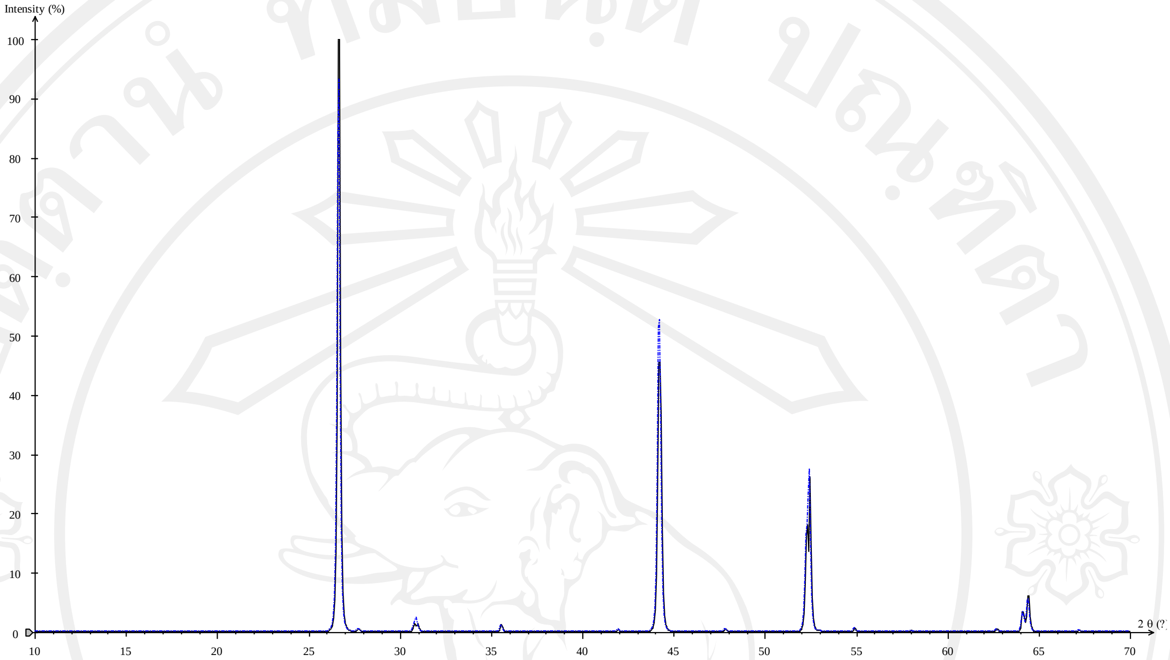

Figure 3.1 The simulation diffraction pattern of $Cu_{0.5}Ag_{1.5}InSe_3$ from CaRIne 3.1

Table 3.1 The simulation diffraction pattern of $Cu_{0.5}Ag_{1.5}InSe_3$ from CaRIne 3.1

No.	(h	k	l)	2-theta	Intensity (%)
1	(1	1	2)	26.65	100.0
2	(2	0	4)	44.18	45.5
3	(2	2	0)	44.28	22.3
4	(1	1	6)	52.27	13.6
5	(3	1	2)	52.43	26.2
6	(3	0	0)	64.12	3.3
7	(4	0	0)	64.41	6.1

The parameters for gel formation were studied. There were temperature, pH, preparing atmosphere, mole-ratio and substrate. The acquired results were reported and discussed as follows.

3.2 Preparation of $Cu_{0.5}Ag_{1.5}InSe_3$(CAIS) gel.

3.2.1 Preliminary results of preparing and annealing temperature.

Both precursor temperatures were used in the preparing process to dissolve all of metal to form homogenous solutions. Moreover, annealing temperature was studied to explore the suitable annealing temperature condition. Annealing was conducted in an air atmosphere.

In table 3.2 showed the SEM results of preparing atmosphere and annealing temperature of CAIS thin films. The results reviewed conditions that particles observed on thin films. In addition, the 25 and 60 refer to preparing temperature, N refer to prepared in nitrogen atmosphere, H refer to water added and Cxxx refer to annealing temperature in air atmosphere.

There were 3 conditions that expected particles (small and round) were observed; CAISN25_C300, CAIS60_C300 and CAISH60_C300 (Figure 3.2). Beside, the EDS results from these samples shown high amount of oxygen in all conditions (Table 3.3). Then the selected condition of CAIS films was CAISN25_C300 conditions, because there was small round homogenous particles support on all area of films. These conditions were used for preparing thin films of CAIS for physical and electrical properties measurements.

Table 3.2 The SEM results of $Cu_{0.5}Ag_{1.5}InSe_3$ preparation in various preparing atmosphere and annealing atmosphere

Condition	Physical Appearance
CAIS25_C300	Round particles support on some area of film.
CAIS25_C400	Round particles support on some area of film.
CAIS25_C500	Non homogenous particle, some particles were aggregated and melt together.
CAISN25_C300	Small round homogenous particles support on all area of film.
CAISH25_C300	Aggregated particle support on some area of films.
CAIS60_C300	Small round homogenous particles support on all area of film. Some area of film found needle shape particle.
CAIS60_C500	Aggregated particle support on some area of films.
CAISH60_C300	Small round homogenous particles support on all area of film.
CAISNH60_C300	Aggregated particle support on some area of films.

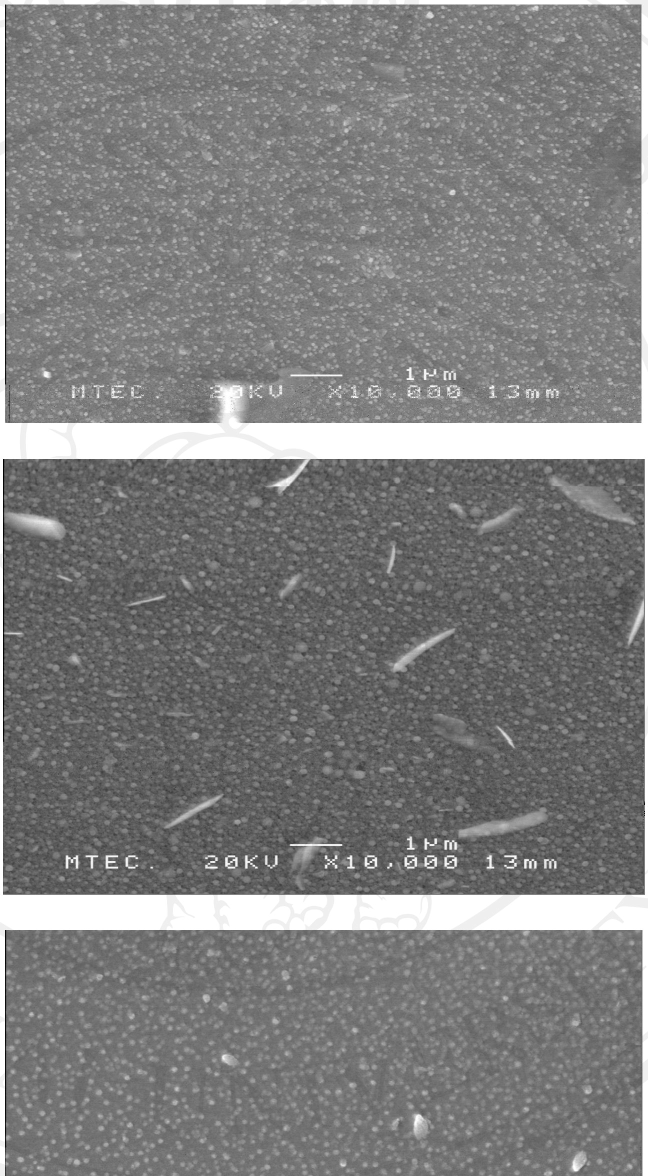

Figure 3.2 SEM images of products from conditions,

a) CAISN25_C300 b) CAIS60_C300 c) CAISH60_C30

Table 3.3 The EDS results of $Cu_{0.5}Ag_{1.5}InSe_3$ preparation in some preparing atmosphere and annealing atmosphere

Conditions	Atomic proportion (%)				
	Cu	Ag	In	Se	O
CAISN25_C300	22.5	1.29	0.33	1.68	58.2
CAIS60_C300	28.0	1.03	0.77	1.59	58.6
CAISH60_C300	16.8	0.09	0.11	0.75	60.3

For all of results were preliminary summarized that high percent of oxygen might be occurred from annealing process. Thus, this reasons lead to approve the annealing atmosphere for the following part.

3.2.2 Results of pH effect

Since the preliminary process found low gel viscosity. So, in this section was showed the improvement gel viscosity process. The pH effect was studied in preparing process. The results were showed in Table 3.4. The results exhibited the effect of pH did not caused the main effect in gelation process. When sulfuric acid was dropped, the viscosity of gel was not changed. Moreover, the addition of sulfuric acid made the dividing into 2 layer of solution. Thus, we can conclude that addition of acid to adjust pH was not approved the gelation process in this study. The selected process to prepare CAIS did not require the addition of acid.

Table 3.4 The result from study pH effect to prepare CAIS gel.

pH	**Viscosity at 25 ^{o}C (Millipascal/sec)**
Diethanolamine	1542
2-propanol	1.95
pH2	27.47
pH3	27.45
pH4	27.10
pH5	27.06
pH6	25.08
pH7	25.11
pH8	24.02
pH9	21.98
pH10	21.02
pH11	20.26

3.2.3 Results of mole ratio

Mole ratios of metal precursor with solvent, stabilizer and water were studied to improved gel viscosity. The study of mole ratios of metal precursor with solvent, stabilizer and water showed the appropriated condition to prepared viscous CAIS gel in Table 3.5.

The mole ratios of precursor with solvent and stabilizer to form gel were 1:40:2 and 1:40:3 moles. The selected ratio was 1:40:2 moles because the viscous of both gels were not different. Then moles ratio of water added in gel were studied and suitable moles ratio of water was obtained. Finally, the condition to form viscous gel of CAIS was Precursor: Solvent: Stabilizer: Water = 1:40:2:1.

Table 3.5 The mole ratios of metal precursor with solvent, stabilizer and water.

Precursor (mole)	**Solvent** (mole)	**Stabilizer** (mole)	**Results**
1	30	0	Some of precursor weren’t dissolved
1	30	2	precipitate
1	30	3	precipitate
1	40	0	Not gel
1	40	2	Gel
1	40	3	Gel

Precursor (mole)	**Water** (mole)	**Results**
1	0	Gel
1	1	Viscous gel
1	2	Gel

3.2.4 Results of the effect of annealing time.

The selected gel condition from 3.2.1 lead to studied of annealing time of CAIS**.** The phase of structure was analyzed by annealing gel to form powder. The CAIS powder was produced by annealing in nitrogen furnace. Annealing time affected the phase of product. In Figure 3.3, D1C300H0 condition was the condition that dried only 1 hour, without annealing. In_2O_3 was observed as the main structure and EDS results (Table 3.8) shown high amount to oxides in sample. No CAIS was observed in other conditions as annealing time increased except D1C300H1 condition.

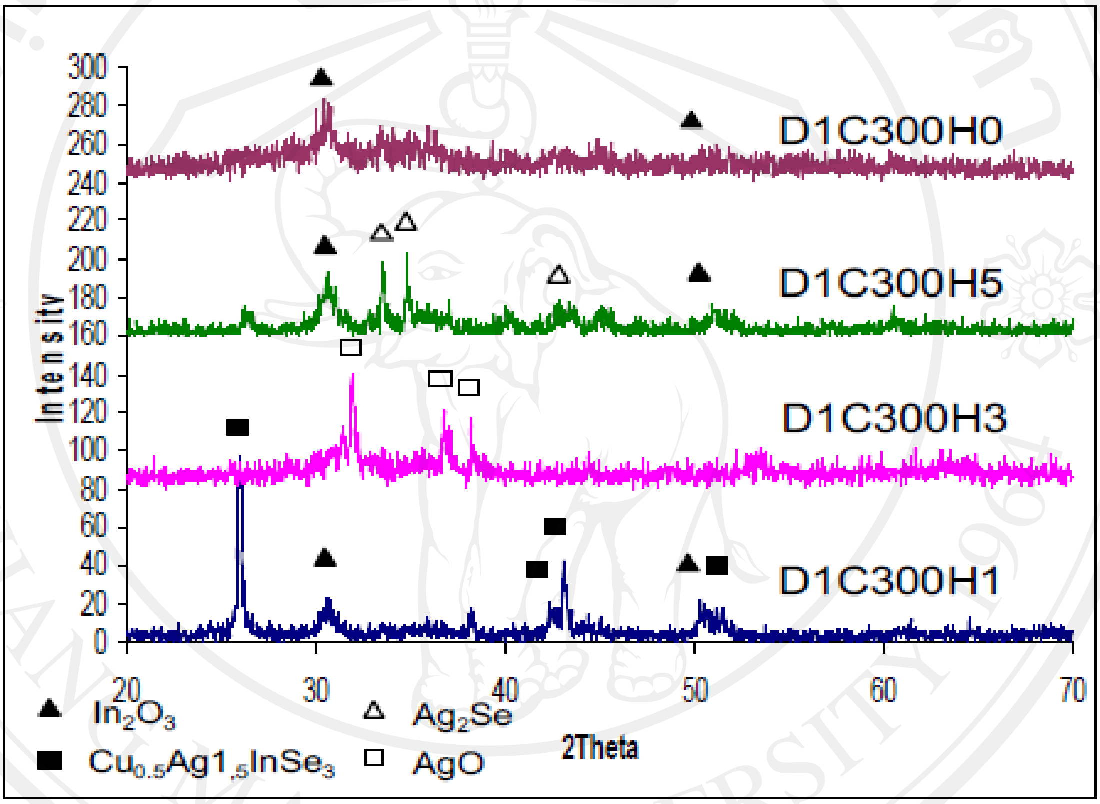

Figure 3.3 The XRD patterns of all synthesized CAIS powders**.**

The SEM images of CAIS powders in various conditions were all similar. Figure 3.4 showed SEM images of D1C300H1 represented all conditions as no particular shape.

Table 3.6 EDS data of $Cu_{0.5}Ag_{1.5}InSe_3$ powder

Conditions	Atomic proportion (%)				
	Cu	Ag	In	Se	O
D1C300H0	3.36	7.64	12.82	17.47	58.71
D1C300H1	3.54	22.56	38.88	24.22	10.80
D1C300H3	17.07	13.15	3.75	8.21	57.83
D1C300H5	1.71	13.92	15.95	11.22	57.20

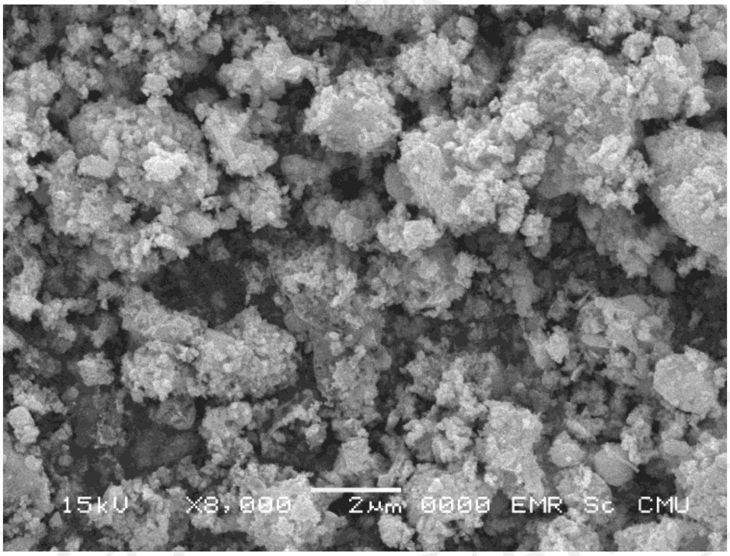

Figure 3.4 The SEM images of synthesized product powders of CAIS in condition D1C300H1.

3.3 Results of the substrate type and times of dip-coating effect.

The substrate effects were studied by two kinds of substrate. In this research glass and alumina substrates were selected. These substrates were mostly used in thermoelectric research. The results of the study were showed in Table 3.7. The gel of CAIS was supported on both substrates and film was developed. In addition, the number of dip-coating times was studied. It was found that both of substrate gave homogenous films before annealing process. The similar of dip-coating times showed the different of film thickness. The film supported on alumina substrate was thicker than on the glass substrate, but after annealing process homogenous film were observed only 1 condition which was 5 times of dip-coating on glass substrate.

Table 3.7 The study of substrate type and times of dip-coating films.

Substrate	Times of dip-coating	CAIS Film (Before anneal)	CAIS Film (After anneal)
Glass	5	Homogenous film	Homogenous film
	10	Homogenous film	Non-homogenous film
Alumina	5	Homogenous film (thicker than glass)	Non-homogenous film (cracked)
	10	Homogenous film (thicker than glass)	Non-homogenous film (cracked)

The appropriate condition to prepare thin films was 5 times of dip-coat on glass substrate. There were non-homogenous and cracked of film on substrates observed in other conditions.

3.4 The TEM results

The phase of $Cu_{0.5}Ag_{1.5}InSe_3$(CAIS) was confirmed with TEM technique by selecting only conditions that OK by XRD technique . The D1C300H1 condition was analyzed and the expected (h k l) of CAIS structure (Figure 3.5) were indexed in ring patterns. The (h k l) data of structure was showed in appendix.

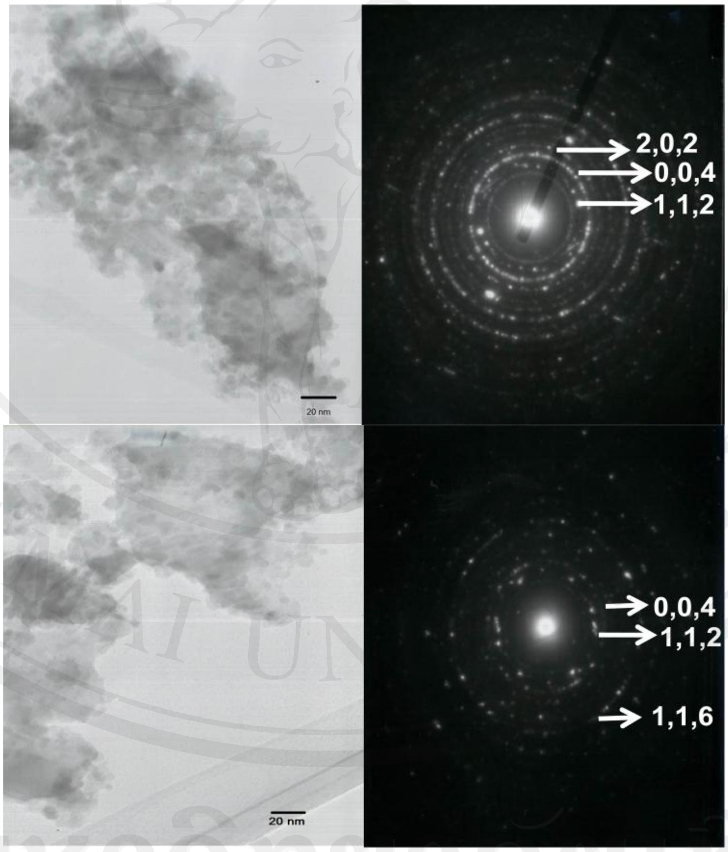

Figure 3.5 TEM image and diffraction pattern of CAIS condition: D1C300H1.

3.5 The electrical conductivity results

The electrical conductivity obtained from Four Point Probe technique. The value of current and voltage that applied to thin film used for calculation by equation 3.1 and 2.1, respectively.

$$\rho = (\pi t / \ln 2)(V/I) \tag{3.1}$$

ρ = Resistivity ($\mu.Ohm.$)

t = Film thickness (cm)

V = Voltage (volt)

I = Current (ampere)

CAIS thickness was analyzed by SEM technique. The thickness was 1.8182 x 10^{-3} cm. When calculated by 3.1 along with 2.1 equations, the results were shown in table 3.8.

Table 3.8 The calculation of electrical conductivity of CAIS films.

No.	**I/V**	**Electrical conductivity** (ohm^{-1}- cm^{-1})
1	2.00 x10^{-5}	2.43 x10^{-3}
2	2.00 x10^{-5}	2.43 x10^{-3}
3	1.00 x10^{-5}	1.21 x10^{-3}
4	1.00 x10^{-5}	1.21 x10^{-3}
Average		1.82 x10^{-3}

3.6 The Seebeck coefficient results

The seebeck coefficient was analyzed by the seebeck coefficient analyzer. The obtained data showed in table 3.11 and figure 3.6

Table 3.9 The seebeck coefficient of CAIS films in different temperature.

Temperature(K)	Seebeck(uV/K)
303.054	0.842
323.017	0.549
342.789	0.436
362.194	0.413
384.765	0.365

Results (Figure 3.6) found that there were positive values of volt when joined positive pole to cold side. It confirmed that CAIS was a p-type semiconductor. In addition, the results showed seebeck coefficient values were decreased when increased the temperature. These results related to D.mardare[37] and Kaymura[38] results by trend of seebeck coefficient with temperature.

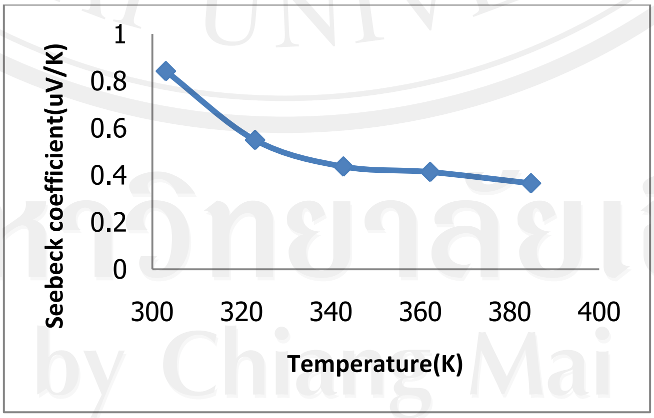

Figure 3.6 The seebeck coefficient of CAIS at various temperatures.

The seebeck coefficient value when compared with Kaymura[38] results found CAIS seebeck coefficient value was lower than another p-type semiconductor at same temperature. Possibly, CAIS was the low temperature semiconductor because it was good properties in lower temperature. In addition, when zinc oxide doped aluminium seebeck coefficient analyzed with the same instrument found 0.198 uV/K. The Sakonakorn seebeck analyzer was analyzed zinc oxide doped aluminium seebeck coefficient 0.244 uV/K. The results showed that the instrument could be a mild error.

$Cu_{0.5}Ag_{1.5}InSe_3$(CAIS) was prepared by sol gel process because it is an easily method when compared with another method. Not complicated instrumentals, method and low temperature process were the advantages of sol gel process. Sol-gel process was consisting of hydrolysis, water condensation and alcohol condensation equations [10].

Hydrolysis : M-O-R + H_2O ------> M-OH + R-OH

Water condensation : M-OH + HO-M ------> M-O-M + H_2O

Alcohol condensation : M-O-R + HO-M ------> M-O-M + R-OH

In these equations, "M" represented "Metal" and "R" represented "Alkyl group" in process. It was showed that gel forming process took only cation gel of metal precursor. Accordingly, CAIS was synthesis.

CAIS was dissolved at only 25^{o}C in ethanol as solvent and diethanolamine as stabilizer. It was good to dissolved at low temperature. The water need to add in the solution to made gelation process (hydrolysis, water condensation and alcohol condensation). Moreover the mole ratio of precursor: solvent: stabilizer: water was affected to the gelation process.

The atmosphere was the core factor in this studied. CAIS need the nitrogen atmosphere in preparing and annealing process. Because in air atmosphere contain oxygen gas that lead to metal oxide formation in samples. The pH was not affected to the gelation process because it not changed the viscous of gel. So, this factor was deleted from process.

CAIS thin films was form on glass substrate and CAIS powder was form by dried for 1 hour and annealed at 300^{o}C for 1 hour. CAIS dried at 279^{o}C because this temperature is the highest boiling point of gel solution (Diethanolamine). Removal diethanolamine by dried at 279^{o}C. The annealing temperature was 300^{o}C was found in report by S. Lee, B. Park [1]. In addition, the process was varying on time of annealing to form CAIS. The results found that for 1 hour at 300^{o}C was formed.

The conductivity of CAIS was conducted. It is mild conducted $(1.82 x 10^{3}$ ohm^{-1}-$cm^{-1})$. Because of it small quantity of CAIS on thin films. Finally, seebeck coefficients of CAIS were decreased when increased the temperature. These results showed CAIS was a low temperature semiconductor that used as thermoelectric material. Conceivably, it up to stabilization of instrument, temperature and technique that used to measured this property.