

The solution route synthesis of the $\text{Cu}_{0.5}\text{Ag}_{1.5}\text{InSe}_3$ compound for thermoelectric applications

Kantapat Chansaenpak* and Thapanee Sarakonsri*

Department of Chemistry, Faculty of Science, Chiang Mai University, 139 Huay Kaew Rd., Muang, Chiang Mai 50200 Thailand

$\text{Cu}_{0.5}\text{Ag}_{1.5}\text{InSe}_3$ compound which is used as a thermoelectric material was successfully synthesized by a simple solution route. The metal ions were reduced simultaneously under alkaline conditions by NaBH_4 . The types of solvent, reaction temperature, indium precursors, and reaction time were studied as the parameters of the synthesis method. The prepared powders were investigated by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and energy dispersive X-ray spectroscopy (EDS). The results show that the reaction temperature is the main factor affecting $\text{Cu}_{0.5}\text{Ag}_{1.5}\text{InSe}_3$ formation. Finally, suitable conditions to prepare $\text{Cu}_{0.5}\text{Ag}_{1.5}\text{InSe}_3$ particles were ethylene glycol as a solvent, 200 degree Celsius as a reaction temperature, indium nitrate as an indium precursor, and 72 h as a reaction time.

Key words: Copper Silver Indium Selenide, Thermoelectric materials, Solution route, Synthesis, Electron microscope.

Introduction

Thermoelectric (TE) materials are normally used in cooling devices and power generators as they can directly convert thermal energy into electricity and vice versa. The thermoelectric efficiency is directly related to the dimensionless figure of merit expressed by the ZT value in which ZT equals $S^2T\sigma/\kappa$ (S = thermopower or Seebeck coefficient, T = temperature, σ = electrical conductivity, and κ = thermal conductivity) [1-3]. However, there are theoretical and experimental studies which have shown that nanostructured TE materials could have higher ZT values compared with the bulk materials [4]. Therefore, the recent promising goal to increase the ZT value is to develop different synthetic methods to prepare TE nanomaterials. Multinary metal chalcogenides have been proposed for prospective applications as thermoelectric materials [5-6]. For example, the new quaternary chalcogenide, $\text{AgPb}_m\text{SbTe}_{2+m}$ [7], has demonstrated effective thermoelectric properties at low and high temperatures with 2.2 as figures of merit (ZT) and it was successfully synthesized by a simple chemical route [8].

$\text{Cu}_{0.5}\text{Ag}_{1.5}\text{InSe}_3$ (CAIS) is a novel class of quaternary chalcogenide compound which is used as a P-type thermoelectric material. CAIS has a tetragonal crystal structure with a space group $I4_2d$ as shown in Fig. 1. Cu/Ag atoms are in $0, 1/2, 1/4$ positions. In atoms are in $0, 0, 1/2$ positions, and Se atoms are in $0.2280, 1/4, 1/8$ positions. Due to the varied structural types that differ considerably from oxides, $\text{Cu}_{0.5}\text{Ag}_{1.5}\text{InSe}_3$, the quaternary chalcogenide compound, is expected to have a high figure of merit.

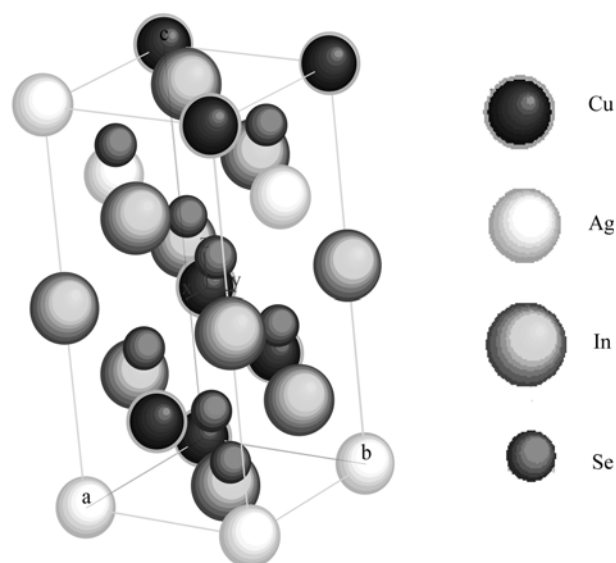


Fig. 1. The $\text{Cu}_{0.5}\text{Ag}_{1.5}\text{InSe}_3$ compound crystal structure simulated by CaRine 3.1 program.

In this study, we use a solution route method to synthesize $\text{Cu}_{0.5}\text{Ag}_{1.5}\text{InSe}_3$ particles. The solution route synthesis gives advantages such as, a low reaction temperature, a fine grain size, and good control of the morphology of the powder [9]. Furthermore, this method has been used to prepare a variety of alloy nanoparticles with high surface area and a dendritic morphology [10]. Recently, thermoelectric nanopowders were successfully synthesized via a chemical solution method [11-14] and an improvement in thermoelectric performance has been obtained. In this simple process, metal ions will be reduced by NaBH_4 under alkaline conditions. The principal benefit of the solution route process is its simplicity because no pressure, vacuum, or large amount

*Corresponding author:
Tel : +66-5394-1907
Fax: +66-5389-2277
E-mail: kantapat_jan@hotmail.com, secchi017@chiangmai.ac.th

of heat are needed [15]. The possible phase formation, particle size, and morphology depend on the conditions of synthesis, which are the solvent, reaction temperature, and reaction time. Moreover, indium precursors were varied to find the most suitable one for the reaction.

Therefore, in this research, $\text{Cu}_{0.5}\text{Ag}_{1.5}\text{InSe}_3$ compound was prepared under various conditions. In order to find a suitable condition, the temperature was varied from room temperature to 200 °C, the solvents were deionized water and ethylene glycol, the indium precursors were indium metal and indium nitrate, and reaction times were 72 and 120 h.

Materials and Methods

All chemical reagents were analytical grade and used without further purification. Product powders were synthesized via a solution route with NaBH_4 (96.0%; Merck) as a reducing agent. 2 g of NaOH (97%; Carlo Erba) was put into a round bottle flask and dissolved in deionized water or ethylene glycol (99.0%; J.T. Baker) by a magnetic stirrer. Then, 1 g of NaBH_4 and 3 mol of Se (99.5%; Merck) were added respectively. The solution was constantly stirred until the mixture color changed to red. In another flask, 1 mol of In precursor (In metal preparing from reducing InCl_3 (96.0%; Fluka) by NaBH_4 or $\text{In}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ (99.0%; Aldrich)), 1.5 mol of AgNO_3 (99.5%; Poch), and 0.5 mol of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (99.5%; Carlo Erba) were dissolved until the solution colour turned blue. The blue solution was ultrasonically agitated for 10 minutes and added drop by drop to the red solution. The mixtures were kept at various temperatures for 12 hour; including, room temperature, 60 °C, 100 °C, and 200 °C. And then, the solutions were held at room temperature for 60 or 108 hours with continuous magnetic stirring. After the reaction was completed, the black powders were washed three times by methanol (100%; J.T. Baker) and dried in oven. All processing parameters were coded and are shown in Table 1.

The phase structure of the powders was analyzed by X-ray diffraction (XRD) on a Siemen D500/D501 polycrystalline X-ray diffractometer using $\text{Cu K}\alpha$. The morphology and elemental analysis was observed by a field emission scanning electron microscope (FESEM) equipped with an energy dispersive X-ray spectrometer (EDS) on a JEOL JSM-5910FE microscope. Nanoscale morphology and its corresponding phase were studied by a transmission electron microscope (TEM) on a JEM-2010 microscope.

Results and Discussions

The XRD patterns of powders obtained from the solution route synthesis at low temperature (room temperature and 60 °C) with indium metal as the indium precursor are shown in Fig. 2. The patterns were compared with the JCPDS file no. 24-1041 corresponding to the Ag_2Se , orthorhombic phase. Nevertheless, tiny peak shifts and slightly different peak intensities were found because of the random

Table 1. Processing parameters for the synthesis of $\text{Cu}_{0.5}\text{Ag}_{1.5}\text{InSe}_3$

order	CODE	Conditions			
		Solvent	Temperature (°C)	Indium precursor	Reaction Time (h)
1	DITRIn72	Deionized water	Room	Indium metal	72
2	DIT60In72	Deionized water	60	Indium metal	72
3	EGTRIn72	Ethylene glycol	Room	Indium metal	72
4	EGT60In120	Ethylene glycol	60	Indium metal	120
5	DITRInN72	Deionized water	Room	Indium nitrate	72
6	EGT60InN72	Ethylene glycol	60	Indium nitrate	72
7	DIT60InN72	Deionized water	60	Indium nitrate	72
8	DIT100InN72	Deionized water	100	Indium nitrate	72
9	EGT200InN72	Ethylene glycol	200	Indium nitrate	72

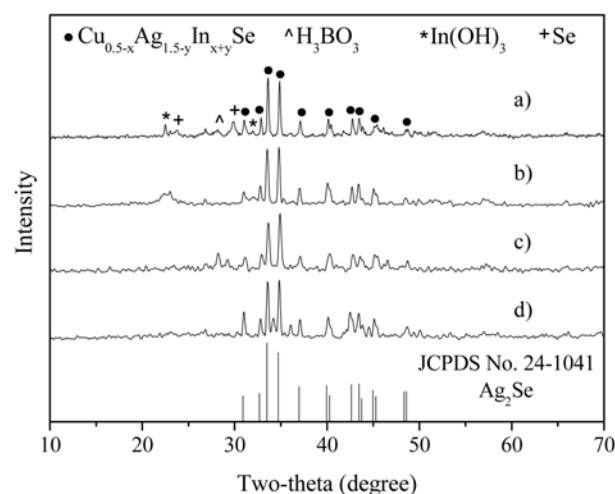


Fig. 2. XRD Patterns of powder synthesized at a low temperature with indium metal as the indium precursor, a) DITRIn72 b) DIT60In72 c) EGTRIn72 d) EGT60In120.

substitution of the Cu and In atoms in Ag atomic positions. Therefore, the orthorhombic phase, $\text{Cu}_{0.5-x}\text{Ag}_{1.5-y}\text{In}_{x+y}\text{Se}$, was assigned as the major product instead of Ag_2Se . All main reflections appeared at 30.906, 32.692, 33.498, 34.729, 36.978, 39.967, 42.633, 43.473, 44.974 degree (2 θ) corresponding to the (102), (120), (112), (121), (013), (103), (113), (201), (032) planes, respectively. Moreover, H_3BO_4 , $\text{In}(\text{OH})_3$, and Se phases were observed as contaminant phases.

The XRD patterns of powders synthesized at low temperature with indium nitrate as the indium precursor are shown in Fig. 3. The results indicated that the $\text{Cu}_{0.5-x}\text{Ag}_{1.5-y}\text{In}_{x+y}\text{Se}$ phase was still observed as the major product at 60 °C whereas the $\text{In}(\text{OH})_3$ phase was found as the major product

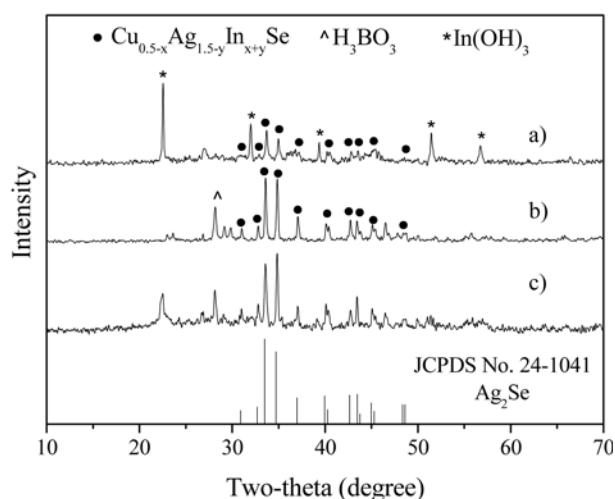


Fig. 3. XRD patterns of powders synthesized at a low temperature with indium nitrate as the indium precursor, a) DITRInN72 b) EGT60InN72 c) DIT60InN72.

at room temperature with deionized water as a solvent. Although indium precursors did not significantly affect $\text{Cu}_{0.5}\text{Ag}_{1.5}\text{InSe}_3$ formation at low temperature, indium nitrate was selected to be used as the precursor at moderate temperatures (100 °C and 200 °C) because of its convenience in use and no toxic gas was formed.

The XRD patterns of powders synthesized at moderate temperatures with indium nitrate as an indium precursor are given in Fig. 4. The results were compared with the pattern from $\text{Cu}_{0.5}\text{Ag}_{1.5}\text{InSe}_3$, tetragonal phase, simulated with the CaRIne 3.1 program. All principal planes appeared at 26.65, 44.18, 44.28, 52.27, 52.43 matching with the (112), (204), (220), (116), (312) planes, respectively. In addition, the amount of $\text{Cu}_{0.5}\text{Ag}_{1.5}\text{InSe}_3$ phase in the products grew with an increase of the synthesis temperature as demonstrated in Fig. 4(b) and 4(c). Although the desired phase was found as the major product at 200 °C, a large

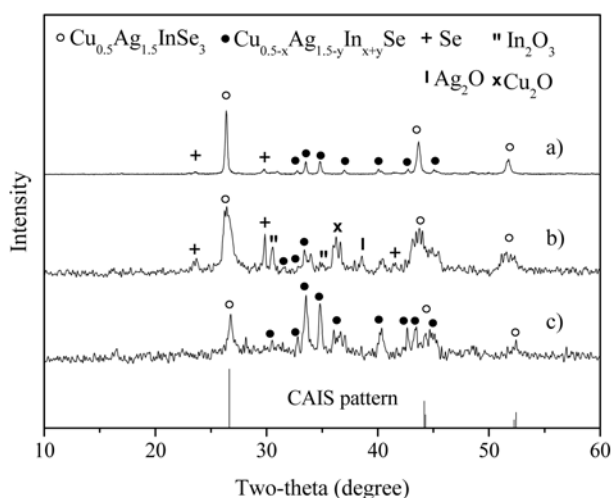


Fig. 4. XRD patterns of powders synthesized at moderate temperatures with indium nitrate as the indium precursor, a) EGT200InN72 after calcination b) EGT200InN72 c) DIT100InN72.

amount of oxide impurities were detected. Eventually, these impure oxides were eliminated by calcination under vacuum at 500 °C for 12 h as shown in Fig. 4(a). The sharp and narrow peaks indicated an increase of crystallization in the product after heating.

From the EDS results given in Table 2, the indium composition was raised with an increase of the synthesis temperature which agrees well with the $\text{Cu}_{0.5}\text{Ag}_{1.5}\text{InSe}_3$ phase formation in the XRD results. This indicates that the indium reaction was stimulated by heat and the $\text{Cu}_{0.5}\text{Ag}_{1.5}\text{InSe}_3$ phase formation was managed by thermodynamic control. However, the Cu, Ag, and Se compositions were not considerably changed when compared between the low temperature synthesis and moderate temperature synthesis.

From the SEM micrographs (Fig. 5), various morphologies were noticed with the different conditions. Although round and agglomerated particles with a particle size ranging from 20 to 100 nm were commonly found in each condition, cubic and rod-shaped particles were observed in some conditions at low temperature. For instance, cubic particles were discovered in the DIT60In72, EGTRIn72, EGT60In120 conditions and rod-shaped particle was observed in the EGT60InN72 condition. This indicates that the morphology of particles can be varied at low temperature. Besides, round and agglomerated morphologies of the product were solely found in the moderate temperature conditions.

As displayed in Fig. 5(d), because of long period preparation process, the particle size in this condition was significantly larger than in the other conditions with a particle size ranging from 300 nm to 1 μm . This signifies that the particle size of powders can be varied by kinetic control in the solution route process.

Fig. 6 shows the TEM morphology and selected area electron diffraction (SAD) pattern of powder prepared in the EGT60In120 condition. The particle shape was elliptical, and the SAD pattern confirmed the existence of the orthorhombic phase of $\text{Cu}_{0.5-x}\text{Ag}_{1.5-y}\text{In}_{x+y}\text{Se}$. Such an observation indicated that $\text{Cu}_{0.5-x}\text{Ag}_{1.5-y}\text{In}_{x+y}\text{Se}$ phase was found at a low temperature as an intermediate phase of $\text{Cu}_{0.5}\text{Ag}_{1.5}\text{InSe}_3$ formation.

Table 2. The EDS results of synthesized products via a solution route

Order	CODE	% weight				
		Cu	Ag	In	Se	O
1	DITRIn72	12.91	19.68	1.48	26.76	29.17
2	DIT60In72	4.25	15.42	1.23	19.33	59.77
3	EGTRIn72	11.69	34.46	1.81	21.53	30.51
4	EGT60In120	7.28	13.33	1.77	13.70	63.93
5	DIT60InN72	9.32	19.58	3.14	27.48	40.48
6	EGT60InN72	12.17	35.92	0.80	44.54	6.57
7	DIT100InN72	2.36	10.75	4.74	11.96	70.19
8	EGT200InN72	12.69	16.80	8.30	38.00	24.21

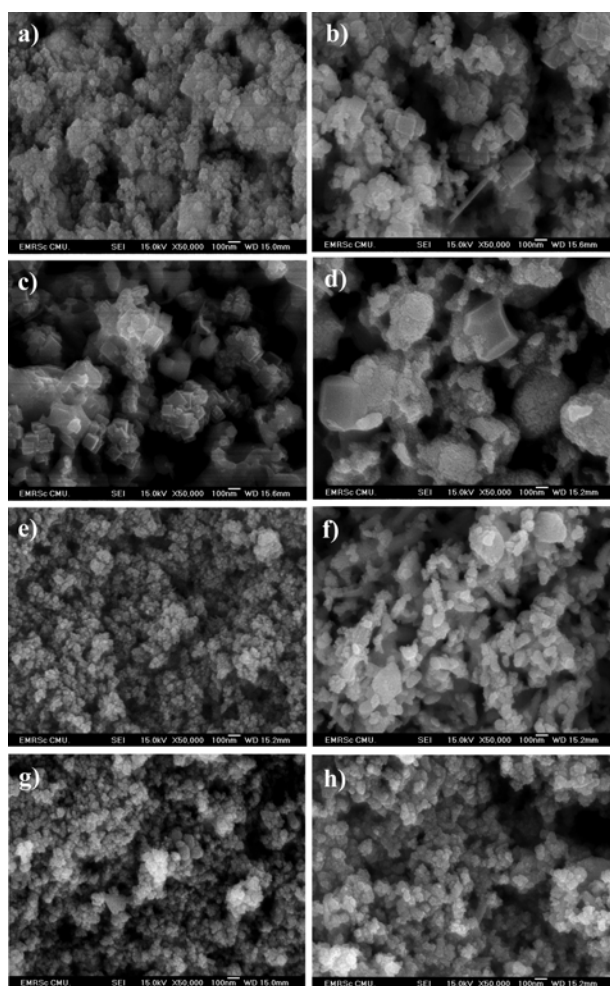


Fig. 5. SEM micrographs of synthesized powders through solution route synthesis, a) DITrIn72, b) DIT60In72, c) EGTrIn72, d) EGT60In120, e) DIT60InN72, f) EGT60InN72, g) DIT100InN72, h) EGT200InN72.

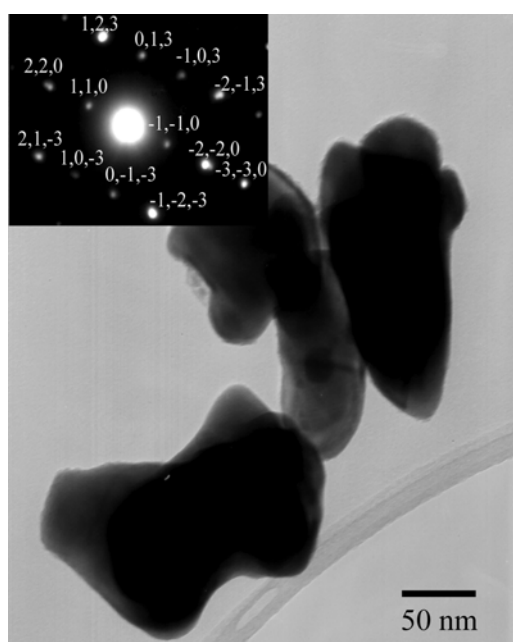
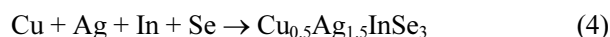
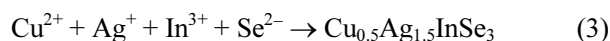
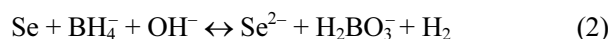
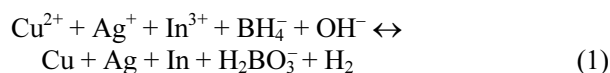


Fig. 6. The TEM micrograph of the product from the EGT60In120 condition.

From the above results from XRD, SEM, EDS, and TEM, a possible reaction mechanism for the preparation of $\text{Cu}_{0.5}\text{Ag}_{1.5}\text{InSe}_3$ compound is proposed as follows:



Based on the standard reduction potentials of each species, $E_{\text{Cu}^{2+}/\text{Cu}}^0 = 0.340 \text{ V}$, $E_{\text{Ag}^+/\text{Ag}}^0 = 0.7996 \text{ V}$, $E_{\text{In}^{3+}/\text{In}}^0 = -0.34 \text{ V}$, $E_{\text{Se}/\text{Se}^{2-}}^0 = -0.67 \text{ V}$, and $E_{\text{H}_2\text{O}/\text{BH}_4^-}^0 = -1.24 \text{ V}$ [16], it provides evidence that the suggested reaction above can be achieved. Due to the reversible processes in reactions (1) and (2), $\text{Cu}_{0.5}\text{Ag}_{1.5}\text{InSe}_3$ powder can be achieved through both mechanisms in reactions (3) and (4) [9, 11]. However, at low reaction temperatures; including, 60°C and room temperature, the reaction of indium species was quite slow because of a lower difference between the standard reduction potential of In^{3+}/In and $\text{H}_2\text{O}/\text{BH}_4^-$. Therefore, at a low synthesis temperature, we noticed that indium was rarely found in the product, and the orthorhombic $\text{Cu}_{0.5-x}\text{Ag}_{1.5-y}\text{In}_{x+y}\text{Se}$ phase was observed. On the other hand, at moderate synthesis temperatures, the reaction of indium was stimulated by heat, and indium atoms were added in larger quantities into the crystal structure. Eventually, the tetragonal $\text{Cu}_{0.5}\text{Ag}_{1.5}\text{InSe}_3$ phase was detected in product powders.

Conclusions

In conclusion, $\text{Cu}_{0.5}\text{Ag}_{1.5}\text{InSe}_3$ or CAIS was successfully synthesized by a simple solution method. The suitable condition to prepare the CAIS phase was EGT200InN72 using ethylene glycol as a solvent, 200°C as a reaction temperature, indium nitrate as indium precursor, and 72 h as reaction time. The XRD and TEM results on phase confirmation indicated that the $\text{Cu}_{0.5-x}\text{Ag}_{1.5-y}\text{In}_{x+y}\text{Se}$ orthorhombic phase was found at low temperatures but the $\text{Cu}_{0.5}\text{Ag}_{1.5}\text{InSe}_3$ tetragonal phase was detected at moderate temperatures. In other words, the amount of CAIS phase was increased with an increase of the synthesis temperature. The EDS results showed the amount of indium was increased when the preparation temperature was raised signify that indium atoms were motivated by the heat to substitute into the crystal structure to form the CAIS phase. The probable mechanism of $\text{Cu}_{0.5}\text{Ag}_{1.5}\text{InSe}_3$ formation had two processes which were atomic combination and ion combination.

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