Journal of Alloys and Compounds 500 (2010) 259–263

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Synthesis of $CdIn_2Se_4$ compound used as thermoelectric materials via the solution method

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ARTICLE INFO

Article history:
Received 17 December 2009
Received in revised form 24 March 2010
Accepted 1 April 2010
Available online 10 April 2010

Keywords:
Cadmium indium selenide
Thermoelectric materials
Solution method

ABSTRACT

$CdIn_2Se_4$ semiconductor is known as a high performance electrical material. In this study, $CdIn_2Se_4$ powder was synthesized via an aqueous chemical reduction, or a solution method, at low temperature, using Se metal, $InCl_3$, and $CdCl_2{\cdot}2.5H_2O$ as precursors, $NaBH_4$ as a reducing agent, and water as a solvent. Preparative parameters have been considered; reaction temperature at 100 and 130 °C, reaction time at 30 min and 6 h. Finally, product powders were characterized by X-ray diffraction, scanning electron microscopy and transmission electron microscopy techniques. The $CdIn_2Se_4$ phase was observed to occur in some preparative conditions with $In(OH)_3$ contaminating phase. However, $In(OH)_3$ impurity has disappeared when the reaction temperature was 130 °C with a reaction time of 30 min, confirmed by XRD patterns. Particle size of product powders was measured from TEM micrographs to be 9.17 ± 0.94 nm.

1. Introduction

Thermoelectric technology is the one of interesting energy sources which needed to be developed due to a fossil fuel deficiency. Important factor influents thermoelectric efficiency of thermoelectric devices is the semiconductor components. General semiconductor materials used in thermoelectric applications are Bi_2Te_3, PbTe, and $Si_{1-x}Ge_x$. Bi_2Te_3 which was commercially available for Peltier coolers or refrigerators shows the highest performance near room temperature. PbTe and $Si_{1-x}Ge_x$ which were used for thermoelectric generator showed the highest performance in upper temperature at 500–600 and above 1000 K, respectively [1].

Cadmium indium selenide is one of the interesting semiconductors due to its optical absorption property with a narrow band gap and a low electrical resistance [2–5]. Because of its narrow band gap, $CdIn_2Se_4$ compound is also widely used in optoelectronic devices [6] and in non-linear optics [7,8]. Based on its notable electrical properties, $CdIn_2Se_4$ is very interesting semiconductor which possibly to be used as thermoelectric generator. Due to its application in micro chip, this compound is always prepared as thin film via many methods such as electro-deposition [9], slurry pasting technique [5], vacuum evaporation [10] and spray pyrolysis [11]. The $CdIn_2Se_4$ thin film that was prepared by an electrical deposition at low temperature has a good optical performance with a narrow band gap [12]. Furthermore, synthesis of $CdIn_2Se_4$ thin film by spray pyrolysis technique obtained a good photovoltaic activity. An obtained thin film has high cystallinity with low electrical resistivity, which lead to high thermoelectric power (S) [13]. Although, $CdIn_2Se_4$ has a good electrical performance, there is also difficulty to prepare as thin film such as, lacking of homogeny in film. Thus, there was an attempt to prepare this material in powder form by a simple method to use as bulk thermoelectric, moreover, powder will feasible for further non-defected thin film preparation.

From the literature survey, there is an interesting report providing the synthesis of thermoelectric material in powder form. Zhu et al. synthesized PbTe thermoelectric material in simple methods by solvothermal, hydrothermal, and alkaline reducing chemical route [14]. The pure phase of PbTe obtained from solvothermal process at 150 °C for 12 h in different solvents which were *N*,*N*-dimethylformamide (DMF), ethylenediamine (en), glycol, acetone, and ethanol. The PbTe products from hydrothermal process using reaction time for 36 h, at temperature 110, 130, 170, and 190 °C were contaminated with Te and PbO phases. However, pure phase observed to occur when the temperature increased to 210 °C. The grain size of PbTe products from solvothermal and hydrothermal process were from tens to hundreds nm. Using the reduction process at low temperature, pure phase of PbTe with grain size of 20 nm obtained at reaction temperature 100 °C and reaction time

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doi:10.1016/j.jallcom.2010.04.023

only 30 min. Therefore, a reduction process at low temperature was superior to the solvothermal and hydrothermal route with many advantages which were short period of reaction time and smaller grain size of product.

In this study, the solution method was used for manipulating $CdIn_2Se_4$ compound. Because it is economical and simple method for preparing thermoelectric materials, especially, $CdIn_2Se_4$ compound in this study. This simple method can be performed in the conventional laboratories with a simply chemical apparatus [14,15].

2. Experimental procedure

2.1. Sample synthesis

In this work, product powders were prepared via the principle of an electron transfer reaction or a redox reaction. Two fractions had been prepared. The first one was an anionic fraction containing Se^{2-} in a basic solution. Another one was a cationic fraction composing of In^{3+} and Cd^{2+} ions dissolved in water. To form the product, the two fractions were mixed in different conditions by varying reaction temperature, reaction time and also amount of reducing agent. The chemical reaction of product formation in the mixed solution is shown in equation below:

$$\text{Mixed solution}: \quad Cd^{2+} + 2In^{3+} + 4Se^{2-} \rightarrow CdIn_2Se_4$$

For an anionic fraction, Se metal was reduced to Se^{2-} by using $NaBH_4$ as a reducing agent in an aqueous basic solution. The preparation began by firstly dissolved NaOH (Thasco, 98%) in de-ionized water and heated at the reaction temperature to warm the basic atmosphere for further complete reduction. After that, Se (Merck, 99.5%) and $NaBH_4$ (Merck, >96%) were added in the solution, respectively. For cationic fraction, two solutions of cationic were prepared by dissolving of $CdCl_2{\cdot}2.5H_2O$ (BDH chemical, Analytical grade) and $InCl_3$ (Fluka, 96%) precursors in de-ionized water separately. After the two solutions were completely dissolved, they were mixed and further sonicated for 10 min. Then, the cationic fraction was added into the anionic fraction giving a homogeneous solution that was left at reaction temperature (100 and 130 °C) and reaction time (30 min, 6 h, and 24 h). After the reactions were finished, the suspensions of the obtained precipitates were sonicated for 30 min and then were left at room temperature. Finally, precipitates were separated from solution by centrifugation and dried overnight in an oven. The flow chart of preparation procedure is shown in Fig. 1. The codes for all preparative conditions are also shown in Table 1.

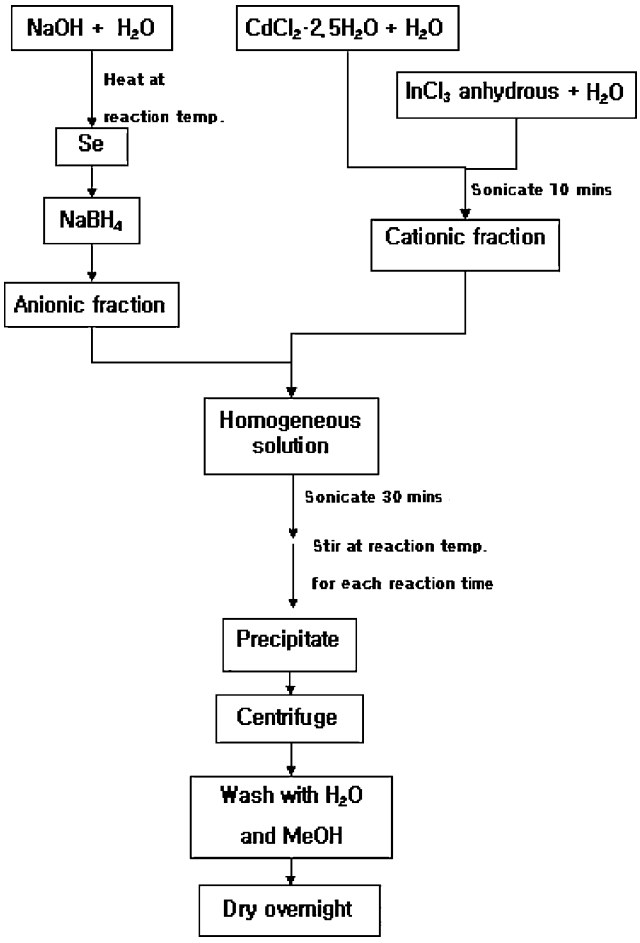

Fig. 1. The experimental flow chart.

2.2. Sample characterization

Product powders were characterized by X-ray diffraction (XRD) technique on SiemenD500/D501 diffractometer to identify phases. Morphology and particle size of product had been analyzed by transmission electron microscopy (TEM; JEOL 2010) technique. Furthermore, composition of product powders was characterized by field emission scanning electron microscopy (FE-SEM; JEOL JSM-5910FE) equipped with energy dispersive spectrometer (EDS) technique.

3. Results and discussion

The results from using the reaction temperature at 100 °C with different reaction times are shown in Fig. 2. The XRD patterns indicated that $CdIn_2Se_4$ product was observed to occur in all preparative conditions, according to the JCPDS no. 79-0835 with three main peaks at 26.528, 44.009, and 52.124 2θ correspond to planes (1 1 1), (2 0 2), and (3 1 1), respectively. However, there were Se and $In(OH)_3$ contaminating phases occurred, indicating by JCPDS no. 73-1810 and JCPDS no. 6-0362, respectively. As shown in the XRD patterns of 100BHE-30 M and 100BHE-6H conditions, Se contaminating phase tended to decrease if increased an amount of reducing agent. The possible reason can be explained as an excess amount of reducing agent may drive the complete forward reduction reaction of Se to Se^{2-}. However, there was a small amount of Se remained, which may be due to the reverse reaction that can thermodynamically occurred.

For all preparative conditions, XRD peaks were broad which possibly because of small particle size of product powders. When the reaction temperature was increased to 130 °C, $In(OH)_3$ and Se contaminating phases disappeared, while $CdIn_2Se_4$ product phase still occurred in all conditions. The 100BHE-30M and 100BHE-6H which

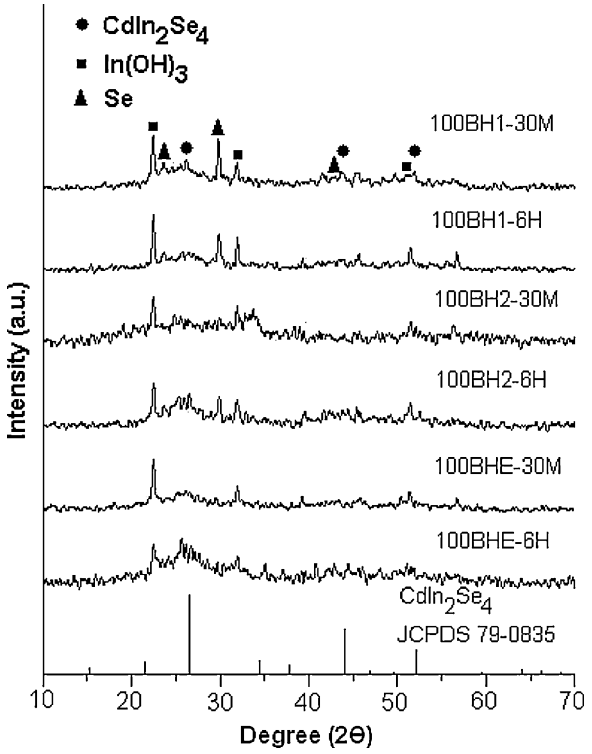

Fig. 2. The XRD patterns of products from conditions synthesized at the reaction temperature 100 °C with different reaction times.

Table 1
Preparative conditions proceeded in the experiment.

No.	Code	Conditions			
		Solvent	Temperature (°C)	Time (h)	Amount of reducing agent (times of e-)
1	100BH1-30M	Water	100	0.5	1
2	100BH1-6H	Water	100	6	1
3	100BH2-30M	Water	100	0.5	2
4	100BH2-6H	Water	100	6	2
5	100BHE-30M	Water	100	0.5	Excess
6	100BHE-6H	Water	100	6	Excess
7	130BH3-30M	Water	130	0.5	3
8	130BH3-6H	Water	130	6	3
9	130BH3-24H	Water	130	24	3

were the condition using a large excess amount of reducing agent, influenced a large decrease of Se contaminating phase. Therefore, these three conditions proceeded at the temperature 130 °C, an amount of reducing agent was adjusted to be 3 times of the required electrons to avoid Se phase formation. Fig. 3 shows XRD pattern of product powders synthesized at temperature 130 °C for different reaction times. For condition 130BH3-6H and 130BH3-24H, there was an amount of Se phase occurred, as shown in Fig. 3. However, from the pattern of 130BH3-30M_2 which was the second time precipitate after the precipitation of the condition proceeded at the reaction time 130 °C, reaction time 30 min, and 3 times of required electrons used (130BH3-30M), pure phase of $CdIn_2Se_4$ product phase was observed. This can be described as a slow precipitation of small colloidal particles containing in the after centrifuged solution.

Product morphology and elemental composition were analyzed by SEM-EDS technique. $CdIn_2Se_4$ phase which was observed to occur in all preparative conditions had a similar morphology which was an accumulated of small particles to a large uncertain shape. Morphology of product from condition 130BH3-30M was the representative for $CdIn_2Se_4$ phase from all conditions that is shown in Fig. 4(a). However, the product from condition 130BH3-30M_2 which was the precipitate from centrifuged solution of condition 130BH3-30M, shown in Fig. 4(b) had different morphology from other conditions. There was a rod structure which seemed to grow out from a group of spherical grains. Although rod morphology was observed to occur (Fig. 5(b)), XRD peaks were still broad that was a result from rod structure growth only on the surface of spherical grains and only in some surface area of sample. Thus, major morphology was still a low crystallinity spherical grain (Fig. 5(a)) which influenced the XRD peak broadening. The EDS results from other conditions are shown in Table 2 which were the average quantities from five random areas measurement. All metal elements, composition of $CdIn_2Se_4$ compound were observed (Table 2).

The TEM results of product powder from condition 130BH3-30M which was the representative of product from all conditions that $CdIn_2Se_4$ was observed, is shown in Fig. 6. Fig. 6(b) is a selected area electron diffraction (SAED) pattern which was indexed as (1 1 1), (2 0 2), and (3 1 1) planes of $CdIn_2Se_4$ compound according to the JCPDS no. 79-0835. This result well agreed with the XRD results. From the TEM image in Fig. 6(a), morphology of product was a small and uncertain shape. Particle size with standard deviation of product was 9.17 ± 0.94 nm, as shown with particle size distribution histogram in Fig. 6(c). Moreover, the high-resolution transmission electron microscopy (HRTEM) was applied to assure the product morphology from condition 130BH3-30M_2. There were two morphologies, rod crystalline and uncertain shape particles, Fig. 7(a) and (b), which diffracted electron beams as spot and ring patterns composed in a diffraction pattern shown in the inset of Fig. 7(a), which confirmed the XRD and SEM results in the previous discussion.

The product powders formation can be described by considering a standard reduction potential (E°) of each specie containing in an aqueous solution. As seen in Eqs. (2)–(4) [16], standard reduction potential (E°) of Se, Cd^{2+}, and In^{3+} are less negative than $NaBH_4$ (Eq. (1)). It is possibly assumed that $NaBH_4$ can reduce all these species in the solution (Eq. (1)).

$$NaBO_2 + 6H_2O + 8Na^+ + 8e^- \rightarrow NaBH_4 + 8Na^+ + 8OH^-, \quad E^\circ = -1.24 \tag{1}$$

$$Se + 2e^- \rightarrow Se^{2-}, \quad E^\circ = -0.67 \tag{2}$$

$$Cd^{2+} + 2e^- \rightarrow Cd, \quad E^\circ = -0.82 \tag{3}$$

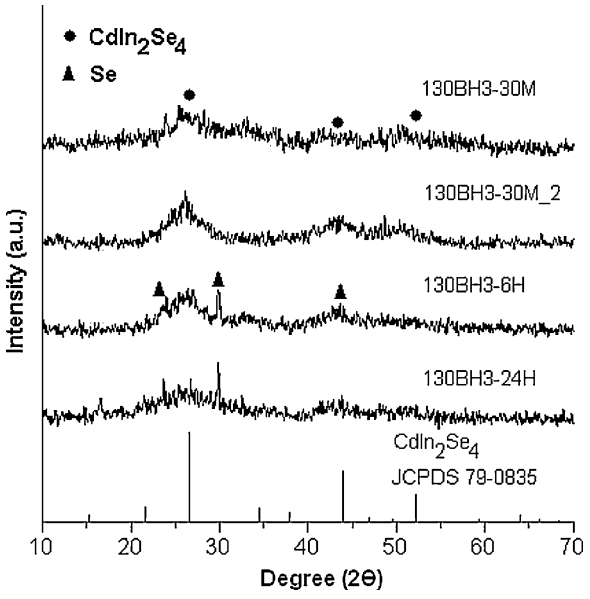

Fig. 3. The XRD patterns of products from conditions synthesized at the reaction temperature 130 °C with different reaction times.

Table 2
Elemental composition observed in synthesized powders from EDS measurement.

No	Codes	Percent by atomic (%)		
		Cd	In	Se
1	100BH1-30M	6.34	12.26	23.08
2	100BH1-6H	7.93	13.44	28.45
3	100BH2-30M	1.14	21.55	2.13
4	100BH2-6H	3.86	15.53	11.86
5	100BHE-30M	8.37	20.75	15.88
6	100BHE-6H	8.22	14.31	20.25
7	130BH3-30M	1.90	11.43	3.63
8	130BH3-30M_2	9.14	12.49	22.35
9	130BH3-6H	7.74	11.39	18.04
10	130BH3-24H	1.72	16.61	2.70

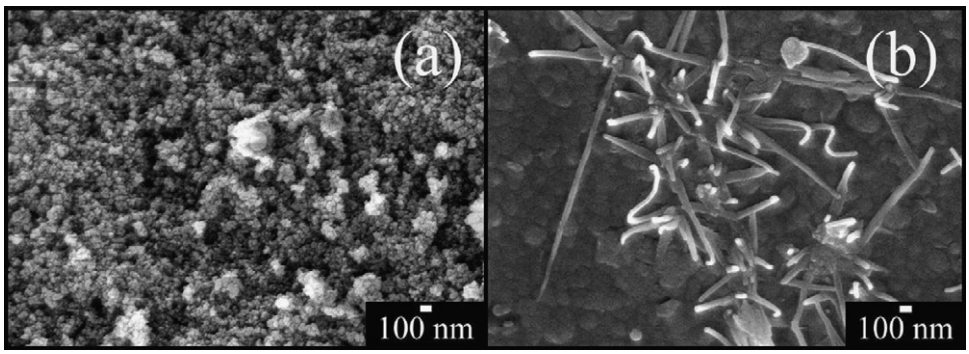

Fig. 4. The SEM images of product powders synthesized by using reaction temperature 130 °C and three times of required electrons of an amount of reducing agent: 130BH3-30M (a) and 130BH3-30M_2 (b).

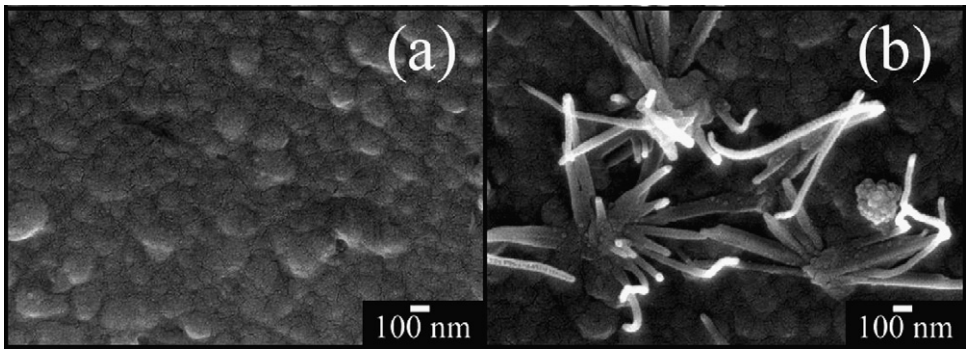

Fig. 5. The SEM images of product powders of condition 130BH3-30M_2 which are spherical structure (a) and rod structure (b).

$$In^{3+} + 3e^- \rightarrow In, \quad E^\circ = -0.34 \tag{4}$$

Two probable mechanisms of $CdIn_2Se_4$ product formation possibly based on the atomic reaction mechanism and the ionic reaction mechanism [14]. In an anion fraction, which Se metal was reduced by $NaBH_4$, might contain both Se and Se^{2-} in form of $Se_{a+1}{}^{2-}$ due to the reversibility of Se^{2-} species in the solution [16], as show in Eqs. (5) and (6). As well as the final homogeneous solution, Cd^{2+} and In^{3+} ions were partly reduced to Cd and In atoms (Eq. (7)). Therefore, product powder possibly formed through both ionic reaction (Eq.

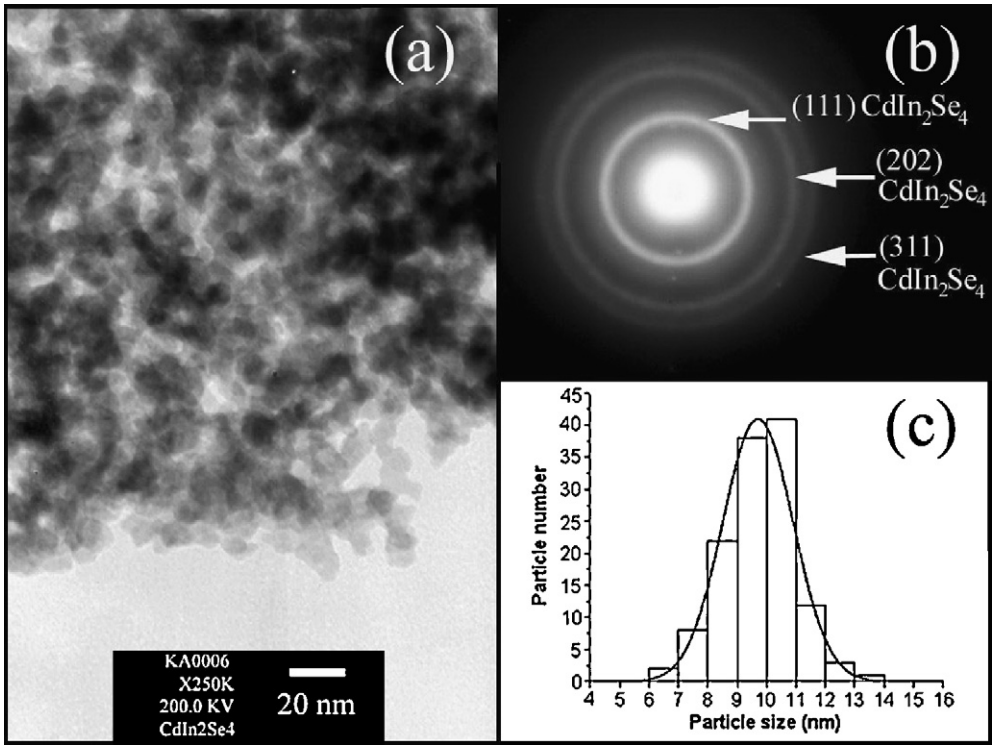

Fig. 6. The TEM image (a), selected area electron diffraction (SAED) pattern (b) and particle size distribution histogram (c) of product powder from condition 130BH3-30M.

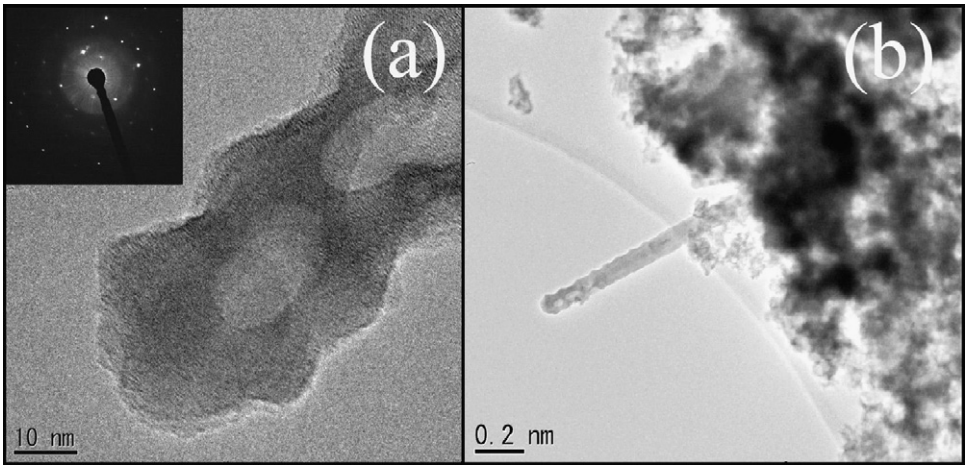

Fig. 7. The high-resolution TEM image of rod structure inserted with selected area electron diffraction (SAED) pattern (a) and TEM image (b) of product powder from condition 130BH3-30M_2.

(8)) and atomic reaction (Eq. (9)), which continued from reactions (6) and (7).

$$BH_4^- + Se + OH^- \rightarrow {Se_{a+1}}^{2-} + H_2BO_3 + H_2 \quad (5)$$

$${Se_{a+1}}^{2-} \leftrightarrow a\text{: } Se + Se^{2-} \quad (6)$$

$$BH_4^- + Cd^{2+} + In^{3+} + OH^- \rightarrow H_2BO_3 + Cd + In + H_2 \quad (7)$$

$$Cd^{2+} + 2In^{3+} + 4Se^{2-} \rightarrow CdIn_2Se_4 \quad (8)$$

$$Cd + 2In + 4Se \rightarrow CdIn_2Se_4 \quad (9)$$

In this experiment, the $CdIn_2Se_4$ product was obtained from all conditions. The products synthesized at the reaction temperature 100 °C obtained $In(OH)_3$ as a contaminating phase. The formation of $In(OH)_3$ phase can be explained by using thermodynamic data. By considering, $\Delta G_f{}^0$ of In^{3+} which is $-97.9\,kJ\,mol^{-1}$ compare with In^0 which is $0\,kJ\,mol^{-1}$. Therefore, free In^{3+} ions are more preferable to form in a solution. Moreover, this experiment was carried out in a basic solution with a plenty of OH^- ions. Thus, In^{3+} ions potentially binded with OH^- ions by ion–ion dipole interaction. From this reason, In^{3+} ions surrounded by OH^- ions are steric. Therefore, it is difficult for electrons to reach In^{3+} specie and reduce to In^0. On the other hand, if the reaction temperature was increased to 130 °C, the $In(OH)_3$ phase disappeared and pure phase of $CdIn_2Se_4$ was obtained. It can be described with kinetic theory that increasing temperature affects molecules to increase their average velocity. High velocity molecules will frequently collide with other molecules. If they collide in suitable direction, leading to high rate of reaction. Therefore, the kinetic energy of In^{3+} ions may increase at high temperature and leads to more product forming.

However, the thermoelectric properties, such as thermoelectric power and electrical resistivity, of the synthesized $CdIn_2Se_4$ compound are necessary for further measurement to assure actual thermoelectric efficiency.

4. Conclusions

$CdIn_2Se_4$ compound was potentially synthesized by a simple reduction method at low temperature using water as a solvent and sodium borohydride as a reducing agent. $CdIn_2Se_4$ product was observed to occur in all of preparative conditions with some impurities. The suitable condition that obtained $CdIn_2Se_4$ pure phase was the condition using three times of required electrons for reduction process, reaction temperature was 130 °C and reaction time for 30 min. Furthermore, particle size of product was 9.17 ± 0.94 nm.

Acknowledgements

The authors would like to thank the Young Scientist and Technologist Programme (YSTP), NSTDA, Ministry of Science and Technology, Thailand, for financial support. Department of Chemistry, Department of Geology, and Chiang Mai University's Electron Microscopy Research and Service Center for laboratory facilities and sample characterization.

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