

CHAPTER 3

RESULTS AND DISCUSSION

3. Result of the AgBiS_2 using a solvothermal method

3.1 Effect of liquid media

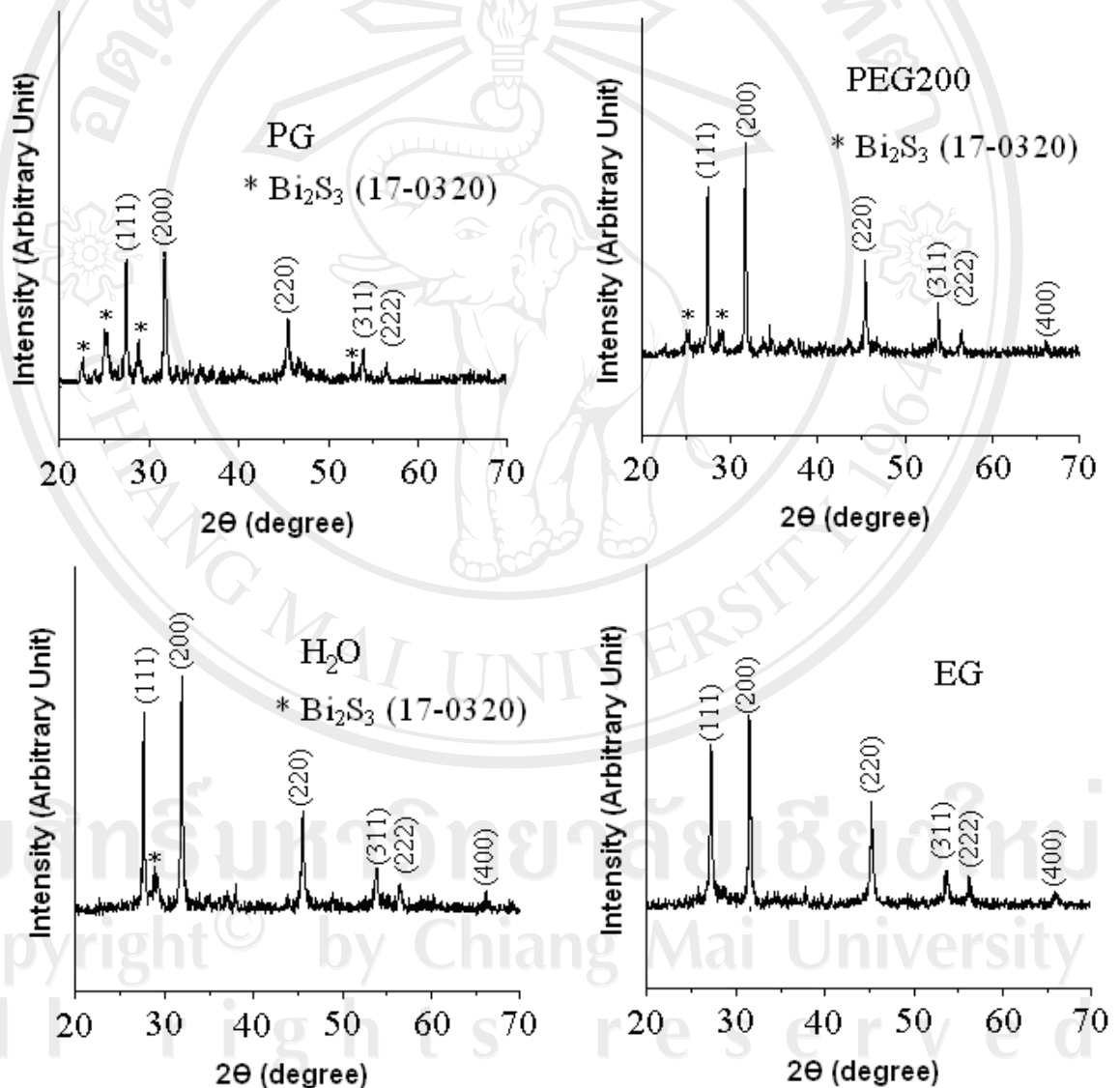


Figure 3.1 XRD patterns of the products synthesized by a solvothermal method

using PG, PEG 200, H_2O , EG as liquid media at 200 °C for 24 h.

Figure 3.1 shows XRD spectra of the products produced in the autoclaves under different conditions. At 200 °C for 24 h in different solvents (PG, PEG 200, H₂O and EG) for 24 h, the products were specified as cubic AgBiS₂ (JCPDS no. 04-0699) [63] with some Bi₂S₃ (JCPDS no. 17-0320) [63] as the impurity — excluding that produced in EG. Its diffraction peaks were narrow and sharp, specifying that the X-ray radiation reflected and diffracted from atoms in lattice order. The strongest intensity peak was at $2\theta = 31.7$ degrees belonging to the (200) plane of the products. In addition, When other solvents (H₂O, PEG 200 and PG) instead of EG were used in the system of 200 °C and 24 h solvothermal reaction, Bi₂S₃ (JCPDS no. 17-0320) [81] as the impurity were produced and detected. . We found that the purities of the products depends on liquid media. These imply that different temperatures and solvents played the role in the product purities.

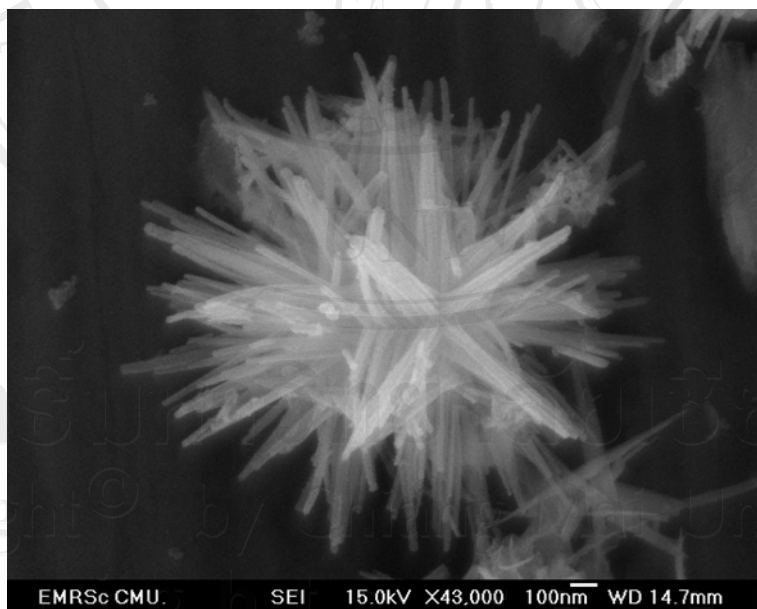


Figure 3.2 SEM image of the sample prepared in polyethylene glycol (PG) solution at 200 °C for 24 h.

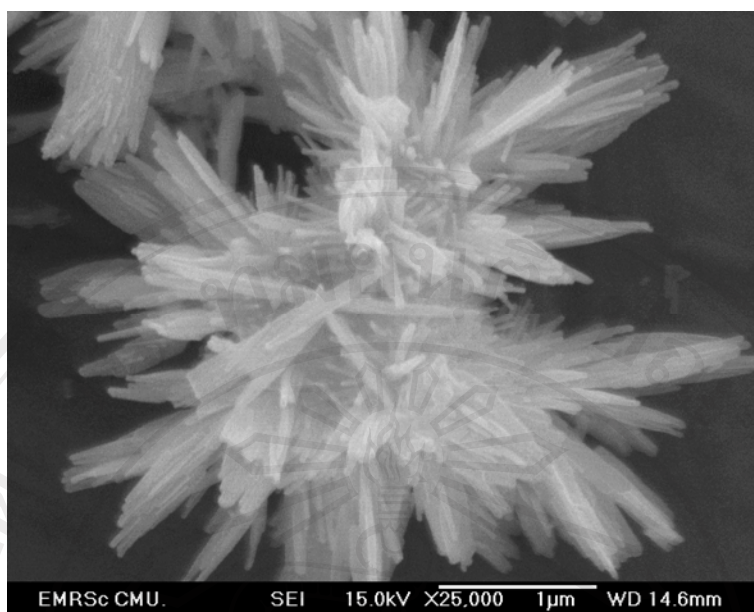


Figure 3.3 SEM image of the sample prepared in polyethylene glycol 200 (PEG 200) solution at 200 °C for 24 h.

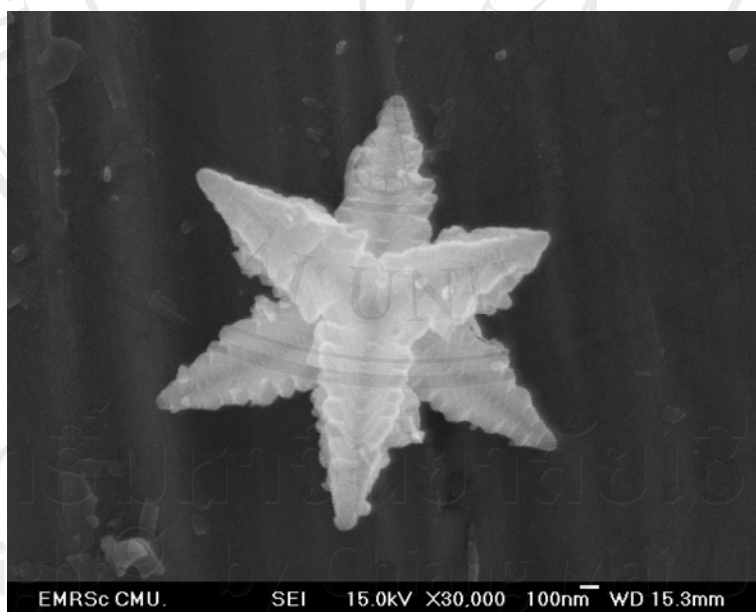


Figure 3.4 SEM image of the sample prepared in water solution at 200 °C for 24 h.

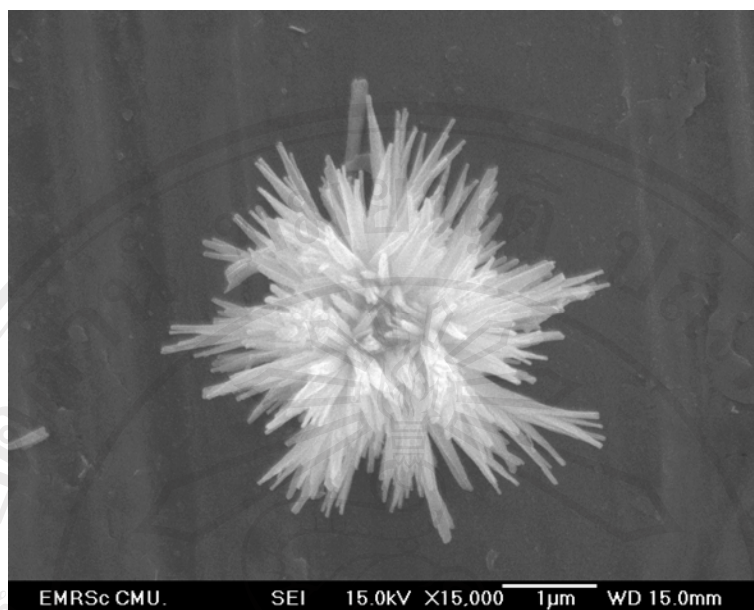


Figure 3.5 SEM image of the sample prepared in ethylene glycol (EG) solution at 200 °C for 24 h.

SEM images of the samples Figures 3.2-3.5 show that morphologies of the products prepared using different liquid media are totally different. In H_2O , a flower-like were detected. A number of short nanorods were synthesized in EG. When other solvents (PEG 200 and PG) instead of EG, the length of nanorods was increased when the molecular weight of solvent increased.

3.2 Effect of temperature

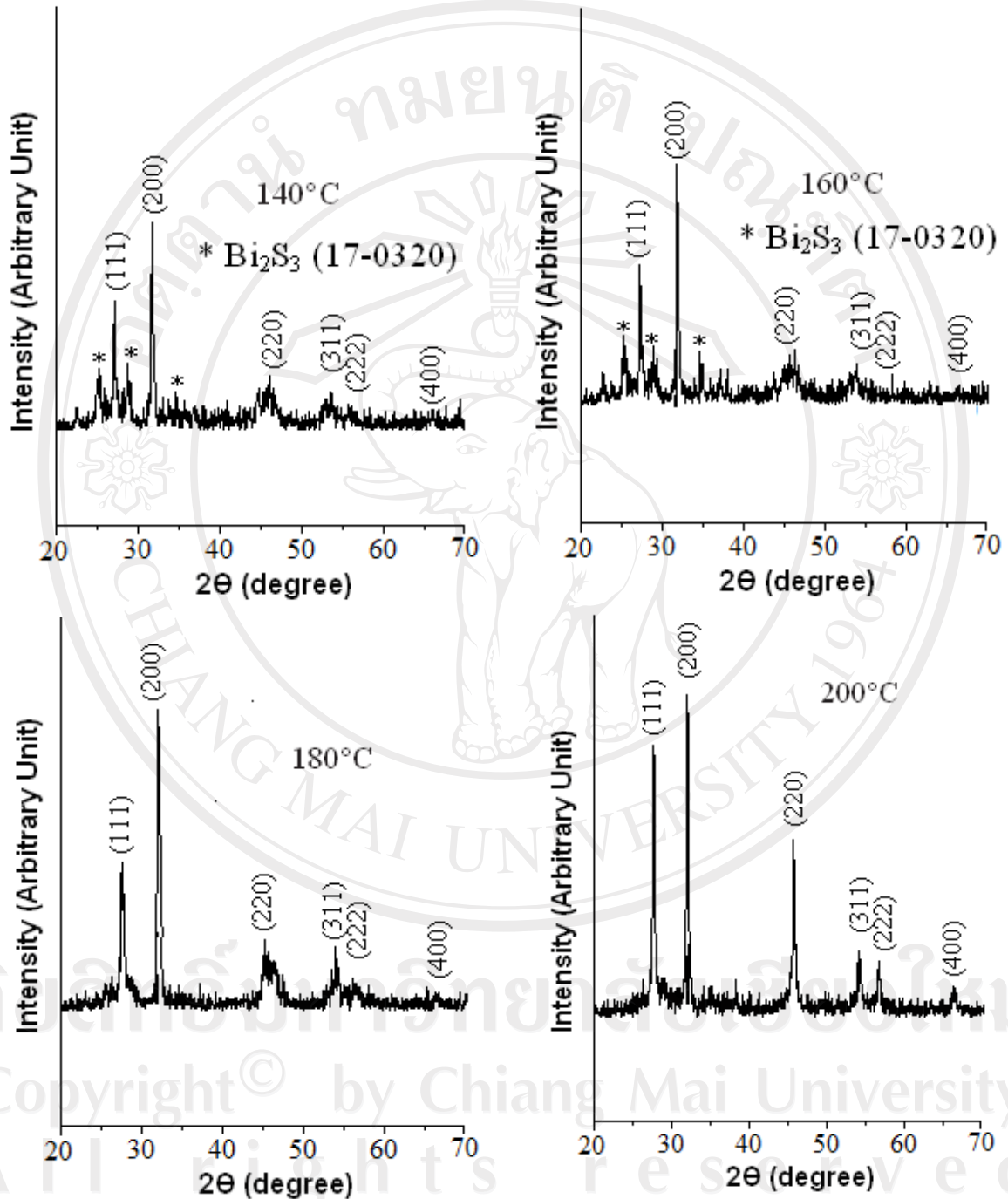


Figure 3.6 XRD patterns of the products in ethylene glycol (EG) solution using chemical reactions proceeded at 140°C, 160°C, 180°C and 200 °C for 24 h.

To save energy consumption, the solvothermal temperature was reduced in a series of steps from 200 °C to 140 °C. It was found that the XRD peaks (Figures 3.6) for the production in EG became broadened— the crystalline degrees of these pure products became lower. These products were no longer pure, when the temperature was lower than 180 °C — some Bi_2S_3 impurity was also detected.

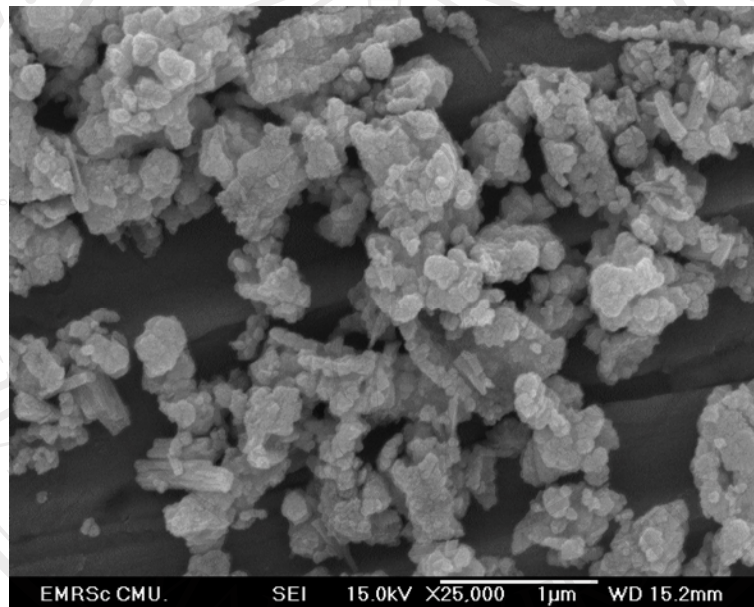


Figure 3.7 SEM image of the products in ethylene glycol (EG) solution using chemical reactions proceeded at 140 °C for 24 h.

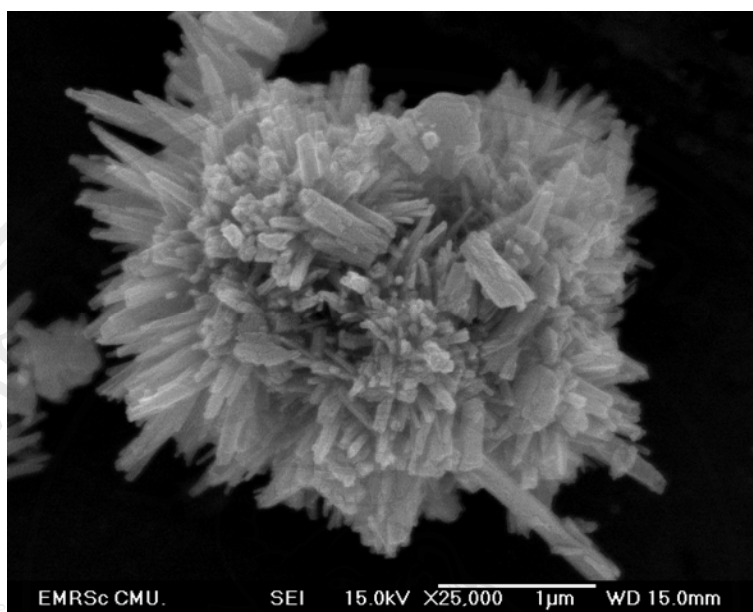


Figure 3.8 SEM image of the products in ethylene glycol (EG) solution using chemical reactions proceeded at 160 °C for 24 h.

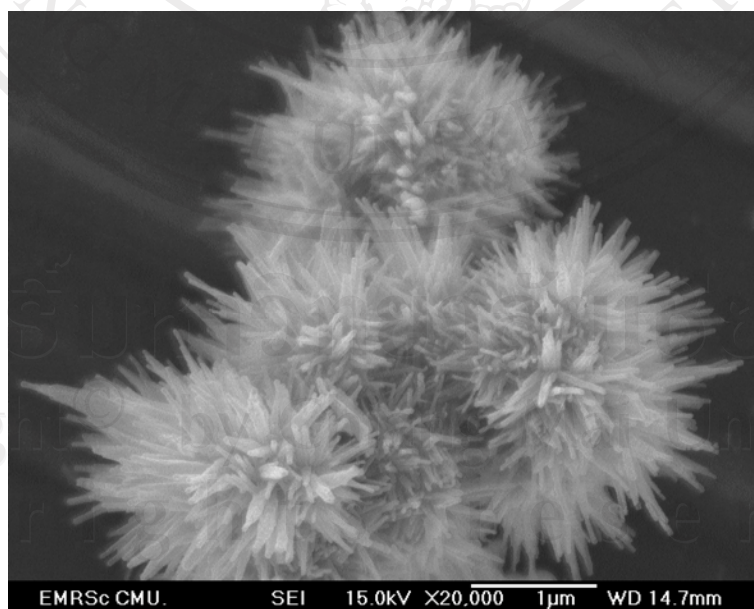


Figure 3.9 SEM image of the products in ethylene glycol (EG) solution using chemical reactions proceeded at 180 °C for 24 h.

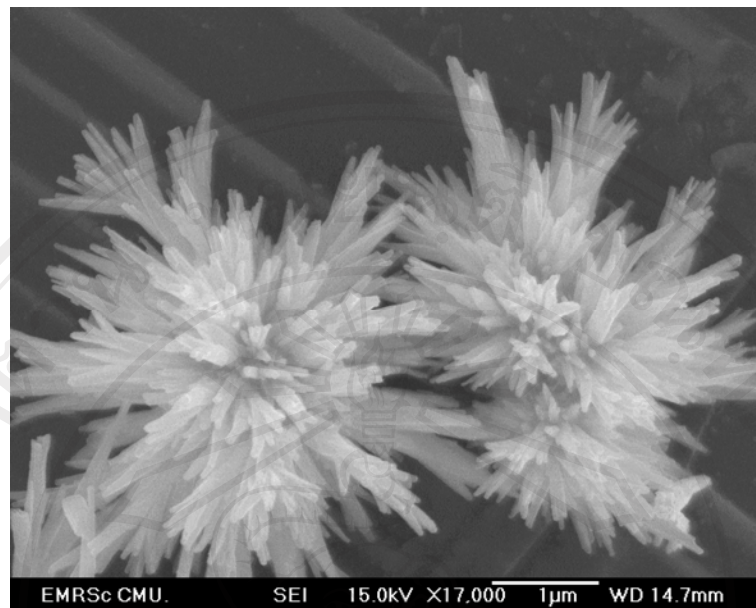


Figure 3.10 SEM image of the products in ethylene glycol (EG) solution using chemical reactions proceeded at 200 °C for 24 h.

SEM images of the samples show nanostructured flowers of AgBiS_2 produced at different temperatures was reduced in a series of steps from 200 °C to 140 °C. It was found that the morphologies of the products prepared using different temperatures are totally different. The products in ethylene glycol (EG) solution using chemical reactions proceeded at 140 °C, a number of nanoparticles were detected (Figures 3.7). A number of short nanorods were synthesized using chemical reactions proceeded at 160 °C (Figures 3.8). The length of nanorods was increased when the increasing temperatures (Figures 3.9-3.10).

3.3 Effect of reaction time

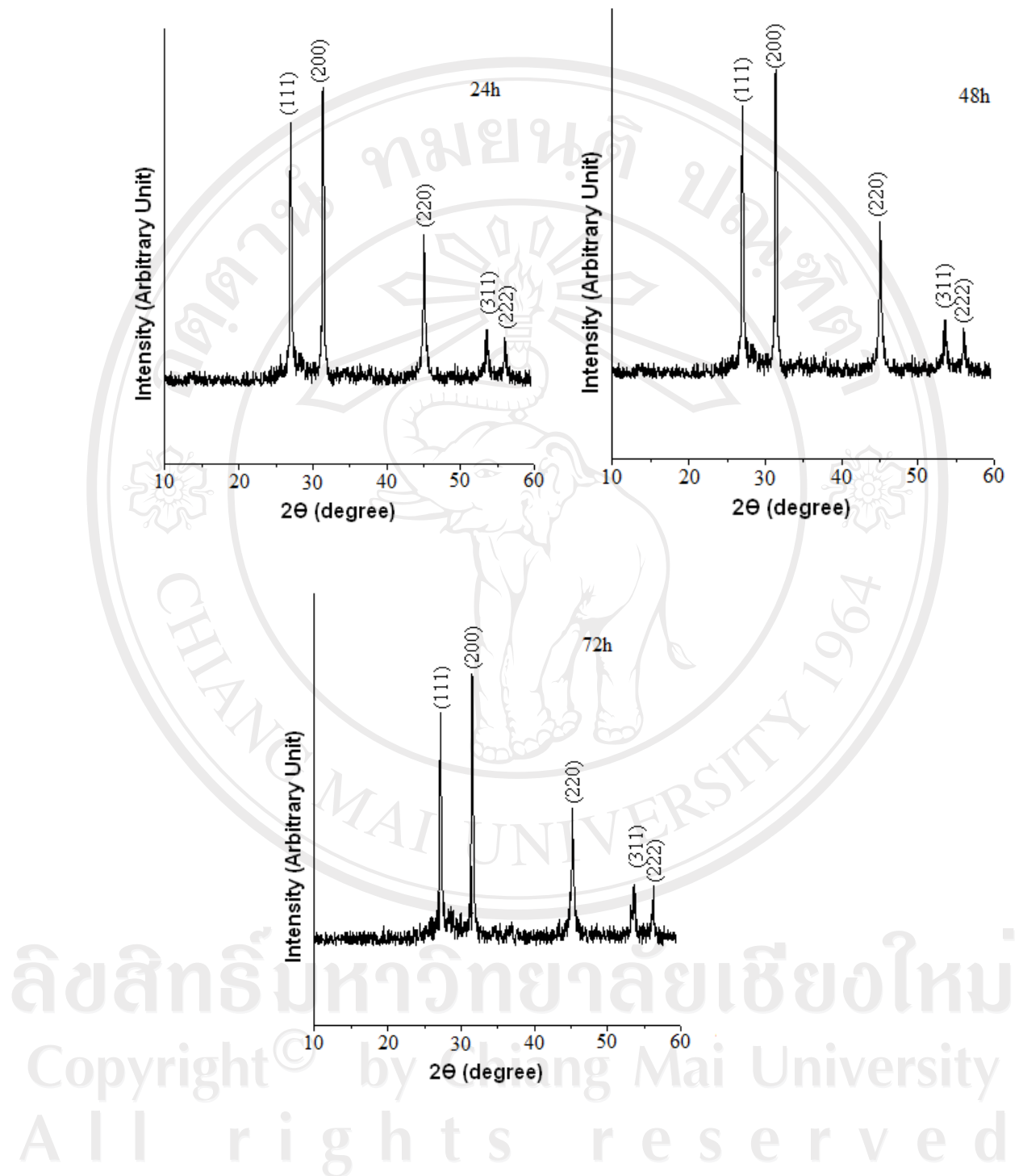


Figure 3.11 XRD patterns of the products in ethylene glycol (EG) solution using chemical reactions proceeded at 200 °C for 24 h, 48 h and 72 h.

At 200 °C and longer time in EG, XRD spectra (Figures 3.11) of the products were very sharp. No peaks of impurities were detected. When increasing reaction time, the intensities of the products became stronger. Thus, we can conclude that the use of EG resulted in high crystallinity of the product. They are independent of the length of time. These imply that both the purity and degree of crystallinity remain unchanged.

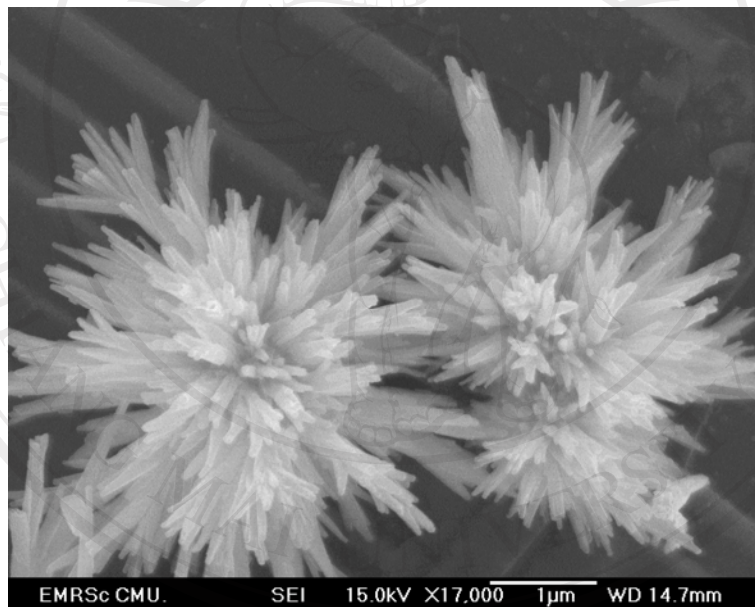


Figure 3.12 SEM image of the products in ethylene glycol (EG) solution using chemical reactions proceeded at 200 °C for 24 h.

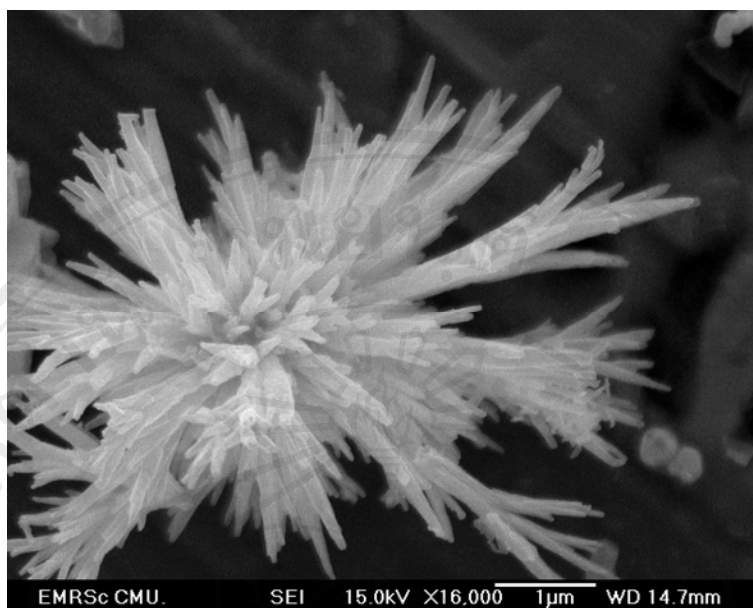


Figure 3.13 SEM image of the products in ethylene glycol (EG) solution using chemical reactions proceeded at 200 °C for 48 h.

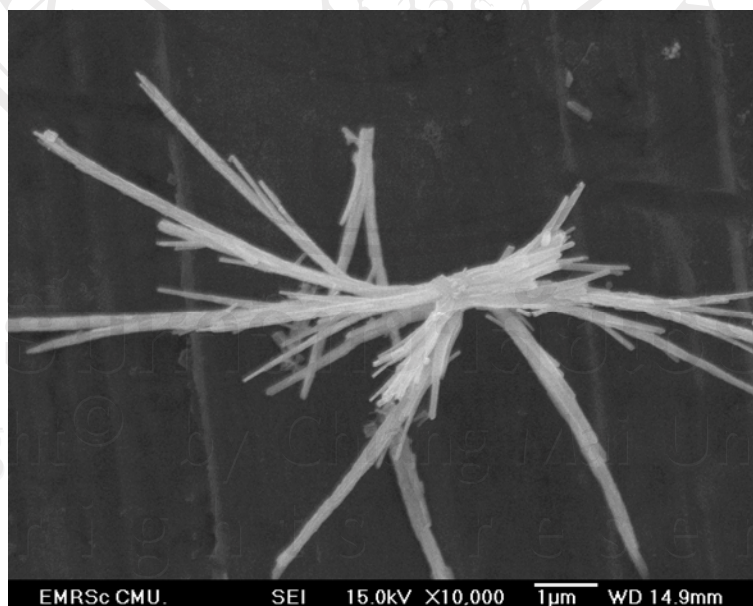


Figure 3.14 SEM image of the products in ethylene glycol (EG) solution using chemical reactions proceeded at 200 °C for 72 h.

SEM images Figures 3.12-3.14 show nanostructured flowers of AgBiS_2 produced at lengths of time. They are totally different from the previous report [18]. Increasing in the temperatures and lengths of time has the influence to enlarge their sizes. Some petals not only became longer and larger, but also have branches.

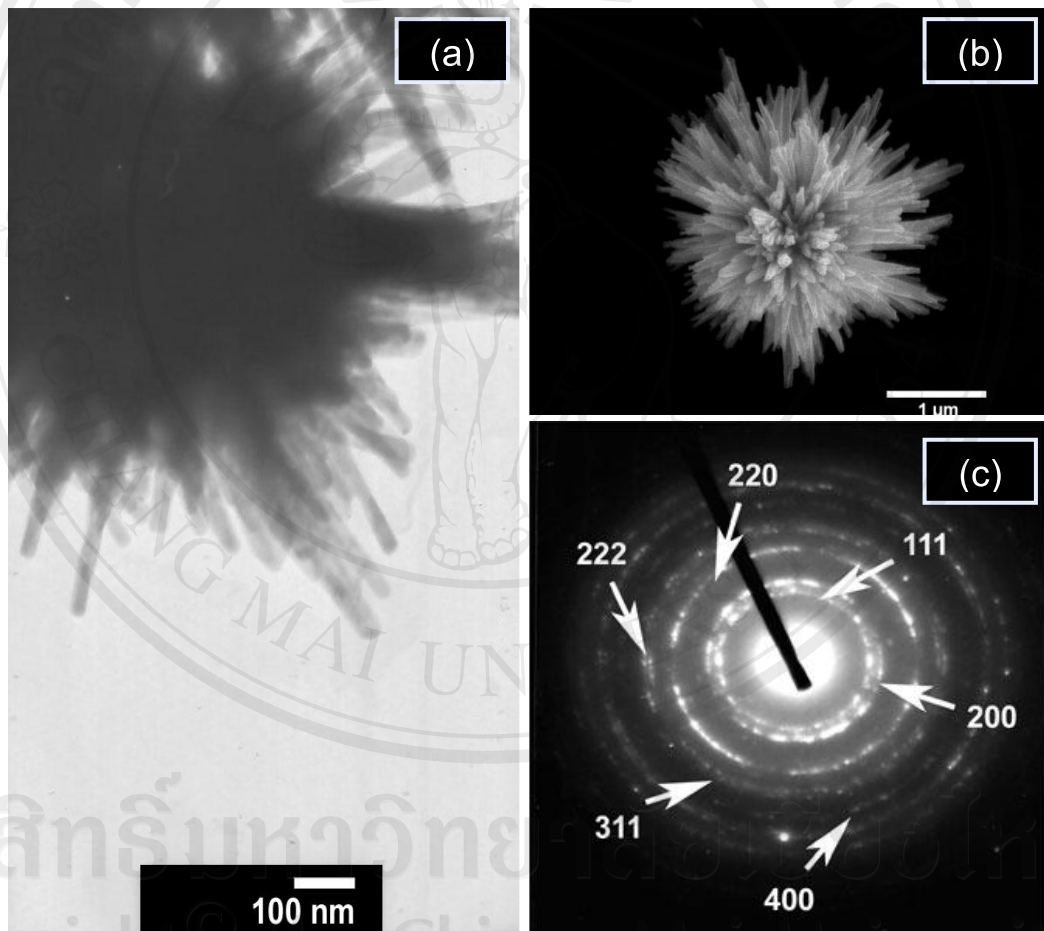


Figure 3.15 SEM , SEAD and TEM image of AgBiS_2 produced in EG (a,b and c) at 200 °C for 24h.

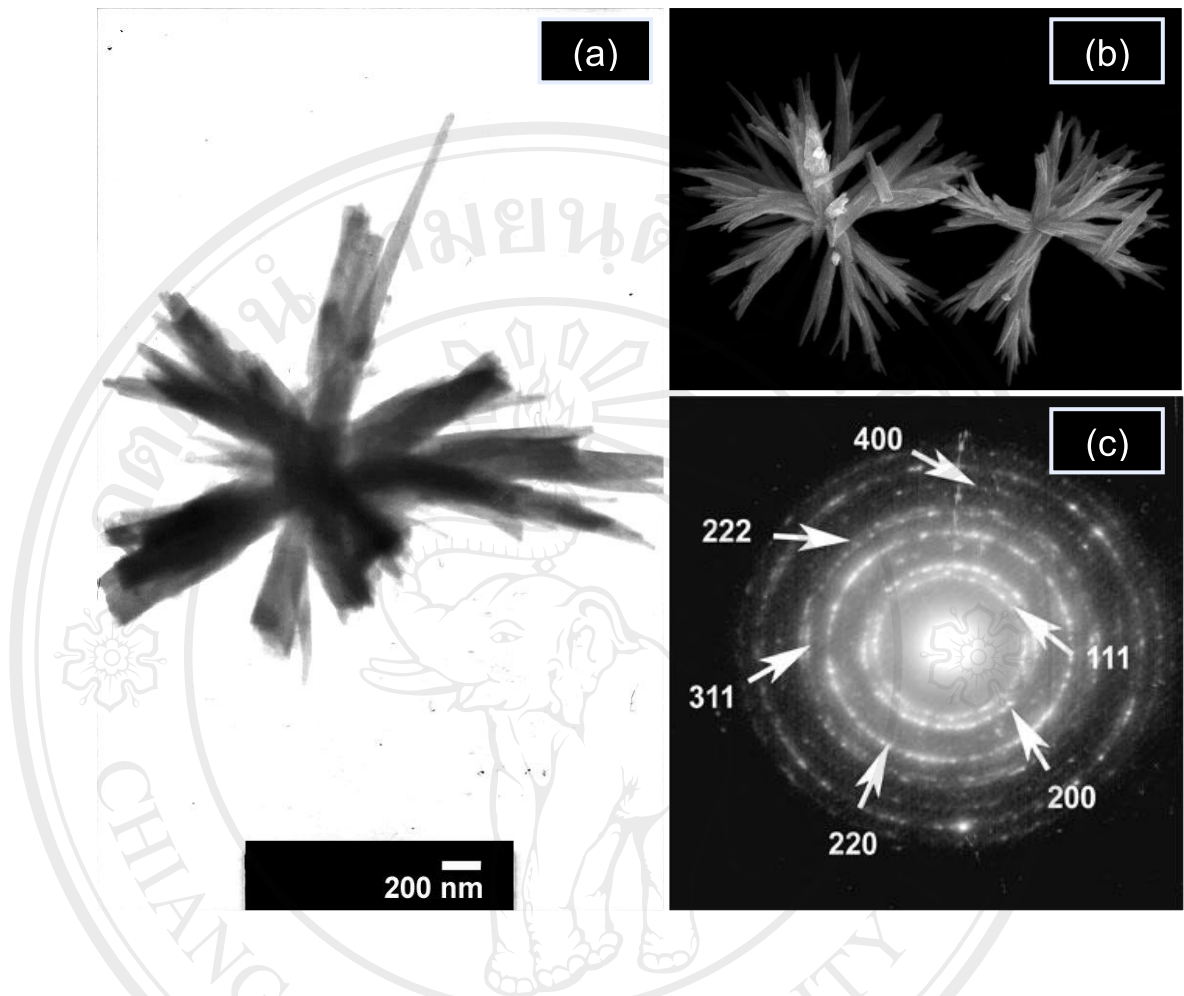


Figure 3.16 SEM , SEAD and TEM image of AgBiS₂ produced in EG (a,b and c) at 200 °C for 48 h.

ลิขสิทธิ์มหาวิทยาลัยเชียงใหม่
Copyright© by Chiang Mai University
All rights reserved

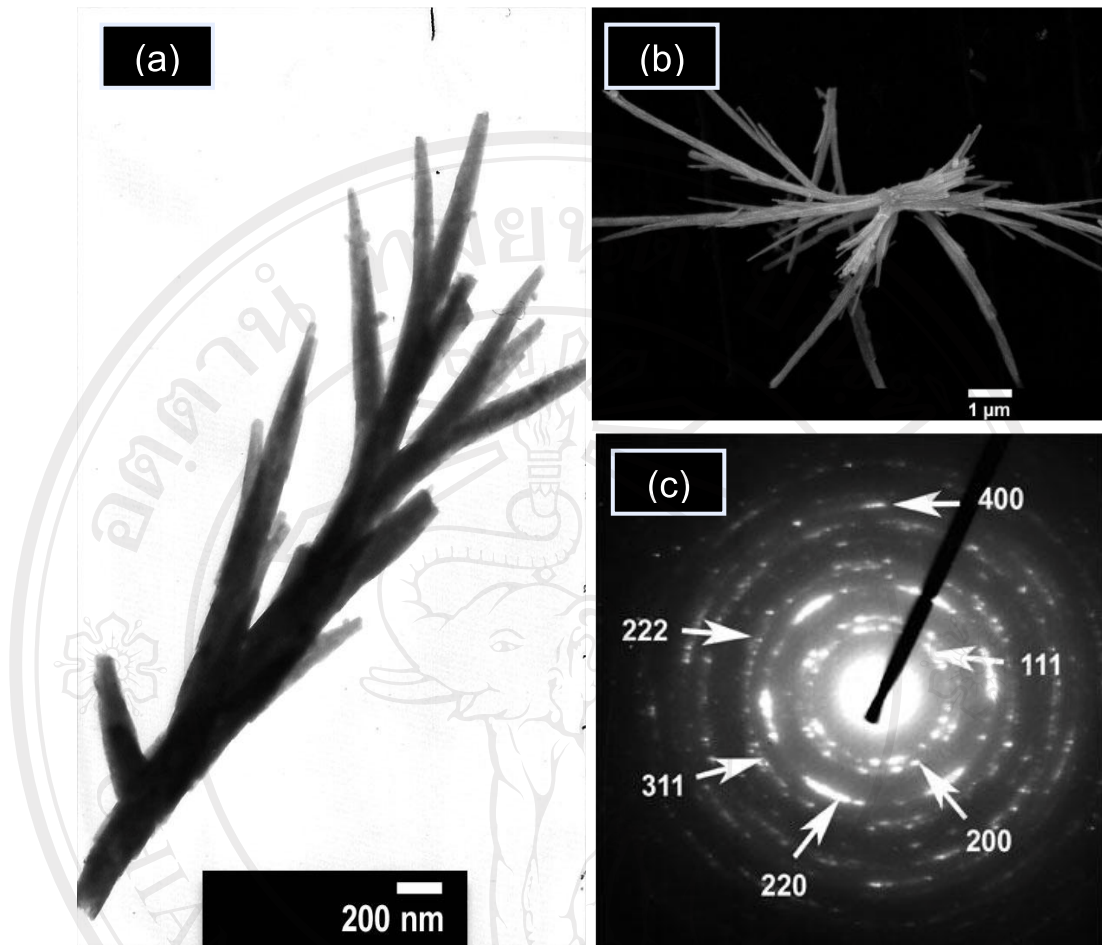


Figure 3.17 SEM , SEAD and TEM image of AgBiS_2 produced in EG (a,b and c) at 200 °C for 72 h.

ลิขสิทธิ์มหาวิทยาลัยเชียงใหม่
 Copyright© by Chiang Mai University
 All rights reserved

Table 3.1 Ring diffraction pattern values of AgBiS₂ prepared in ethylene glycol at 200 °C for 24 h.

Ring No.	Diameter (mm)	Radius (mm)	Calculated d-spacing (Å)	d-spacing (JCPDS 04-0699)	Plane hkl		
					h	k	l
1	15.4	7.70	3.24	3.24	1	1	1
2	17.8	8.90	2.80	2.82	2	0	0
3	25.2	12.61	1.98	1.98	2	2	0
4	29.6	14.80	1.69	1.69	3	1	1
5	30.5	15.25	1.64	1.63	2	2	2
6	35.4	17.71	1.41	1.41	4	0	0

Table 3.2 Ring diffraction pattern values of AgBiS₂ prepared in ethylene glycol at 200 °C for 48 h.

Ring No.	Diameter (mm)	Radius (mm)	Calculated d-spacing (Å)	d-spacing (JCPDS 04-0699)	Plane hkl		
					h	k	l
1	15.4	7.70	3.24	3.24	1	1	1
2	17.7	8.85	2.82	2.82	2	0	0
3	25.2	12.61	1.98	1.98	2	2	0
4	29.7	14.85	1.68	1.69	3	1	1
5	30.5	15.25	1.64	1.63	2	2	2
6	35.6	17.80	1.40	1.41	4	0	0

Table 3.3 Ring diffraction pattern values of AgBiS₂ prepared in ethylene glycol at 200 °C for 72 h.

Ring No.	Diameter (mm)	Radius (mm)	Calculated d-spacing (Å)	d-spacing (JCPDS 04-0699)	Plane hkl		
1	15.4	7.70	3.24	3.24	1	1	1
2	17.7	8.85	2.82	2.82	2	0	0
3	25.2	12.61	1.98	1.98	2	2	0
4	29.5	14.77	1.69	1.69	3	1	1
5	30.7	15.35	1.63	1.63	2	2	2
6	35.7	17.71	1.41	1.41	4	0	0

SEM and TEM images Figure 3.15-3.17 show nanostructured flowers of AgBiS₂ produced at different temperatures and lengths of time. They are totally different from the previous report [18]. Increasing in the temperatures and lengths of time has the influence to enlarge their sizes. Some petals not only became longer and larger, but also have branches. High magnification TEM image (Figure 3.18b) of a petal produced at 200 °C for 24 h shows a number of parallel lattice planes with 3.19 Å apart, corresponding to the (111) crystallographic plane of the product. A SAED pattern (Figure 3.15c) of the product with 200 °C and 24 h reaction composed of a number of bright spots, arranged in concentric circles. These circles are diffuse and hollow, implying that the product is poly-nanocrystals. Another SAED pattern (Figure 3.18c), which is in good accordance with that of the simulation [64]—

systematic and symmetric array of dark spots (Figure 3.18d), appears as light spots of diffraction electrons from a single crystal with the $[-112]$ direction as zone axis. They (Figure 3.15c and 3.18c) were indexed [65] and specified as cubic AgBiS_2 (JCPDS no. 04-0699) [63].

To produce AgBiS_2 , CH_3COOAg and $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ in ethylene glycol (EG) were mixed to form a mixture, to which thiosemicarbazide ($\text{NH}_2\text{CSNHNH}_2$) in EG was subsequently added. At this stage, Ag^+ and Bi^{3+} ions reacted with thiosemicarbazide (TBZ) at room temperature to form complexes [15,16].



These complexes were decomposed by the 200°C solvothermal reaction in EG. Due to the stability of the complexes, the reaction proceeded with rather slow rate — the number of nuclei was less than that produced by the direct ion-exchange reaction [16]. $(\text{AgBiS}_2)_n$ nuclei were produced, and finally transformed into AgBiS_2 [15] — detected by XRD analysis.



The decomposition rates of these two complexes are appropriate to the production of AgBiS_2 without any impurities. In general, the decomposition rates of the complexes are different, controlled by the temperatures and pressures. When the solvothermal reaction was done at lower temperature, the decomposition rates of these two complexes became slow down. The final products remain unchanged although the temperature was as low as 180°C . At 200°C and 180°C , molar ratio of Ag^+ and Bi^{3+} , obtained from the decomposition of the complexes, was very closed to 1:1, and sulfur in the solution was either in excess or exactly right to the product formation.

Thus AgBiS_2 was produced and detected by XRD analysis. When the research was done at $160\text{ }^\circ\text{C}$ or $140\text{ }^\circ\text{C}$, the decomposition rate of Ag-TBZ complexes seemed to be less than that of Bi-TBZ complexes. Thus Ag^+ of the complex decomposition was used up. But for Bi^{3+} and sulfur, they were left in the solution, and additional Bi_2S_3 was produced and detected. It is worth to note that AgBiS_2 formation was influenced by the concentrations of Ag^+ , Bi^{3+} and sulfur obtained from the decomposition process, and the product purity was controlled by the slowest process.

When other solvents (H_2O , PEG 200 and PG) instead of EG were used in the system of $200\text{ }^\circ\text{C}$ and 24 h solvothermal reaction, both AgBiS_2 and Bi_2S_3 were produced and detected. These imply that different temperatures and solvents played the role in the product purities.

Due to the $200\text{ }^\circ\text{C}$ and $180\text{ }^\circ\text{C}$ solvothermal reactions for 24 h in EG, AgBiS_2 nanostructured flowers were produced by the orientation growth [15,16]. During growing, the process was anisotropic and the flowers were produced. As the time was lengthened, atoms had more chance to adsorb on the petals to enlarge their size. Concurrently, new young branches had also initiated to grow out from these main petals.

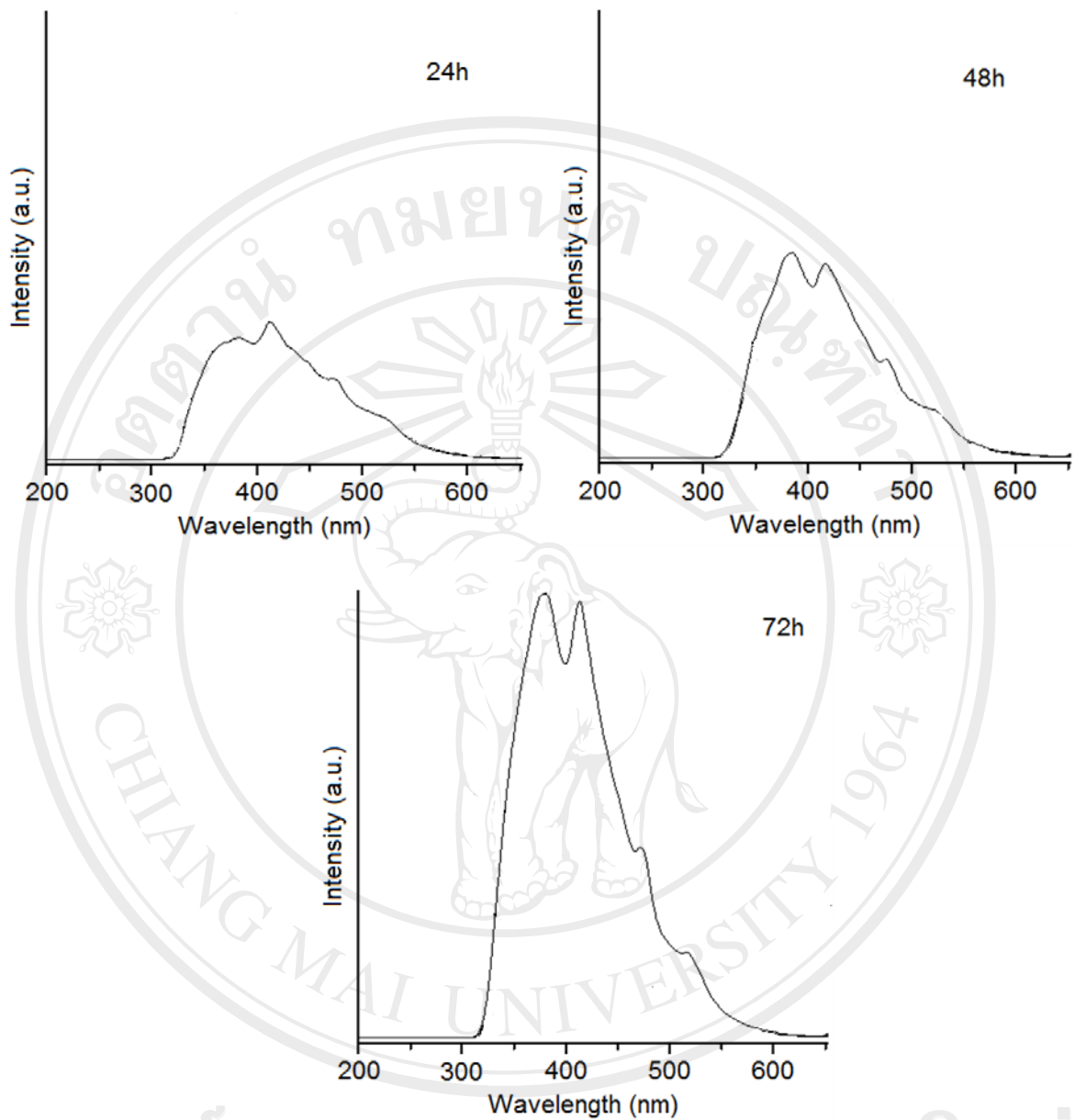
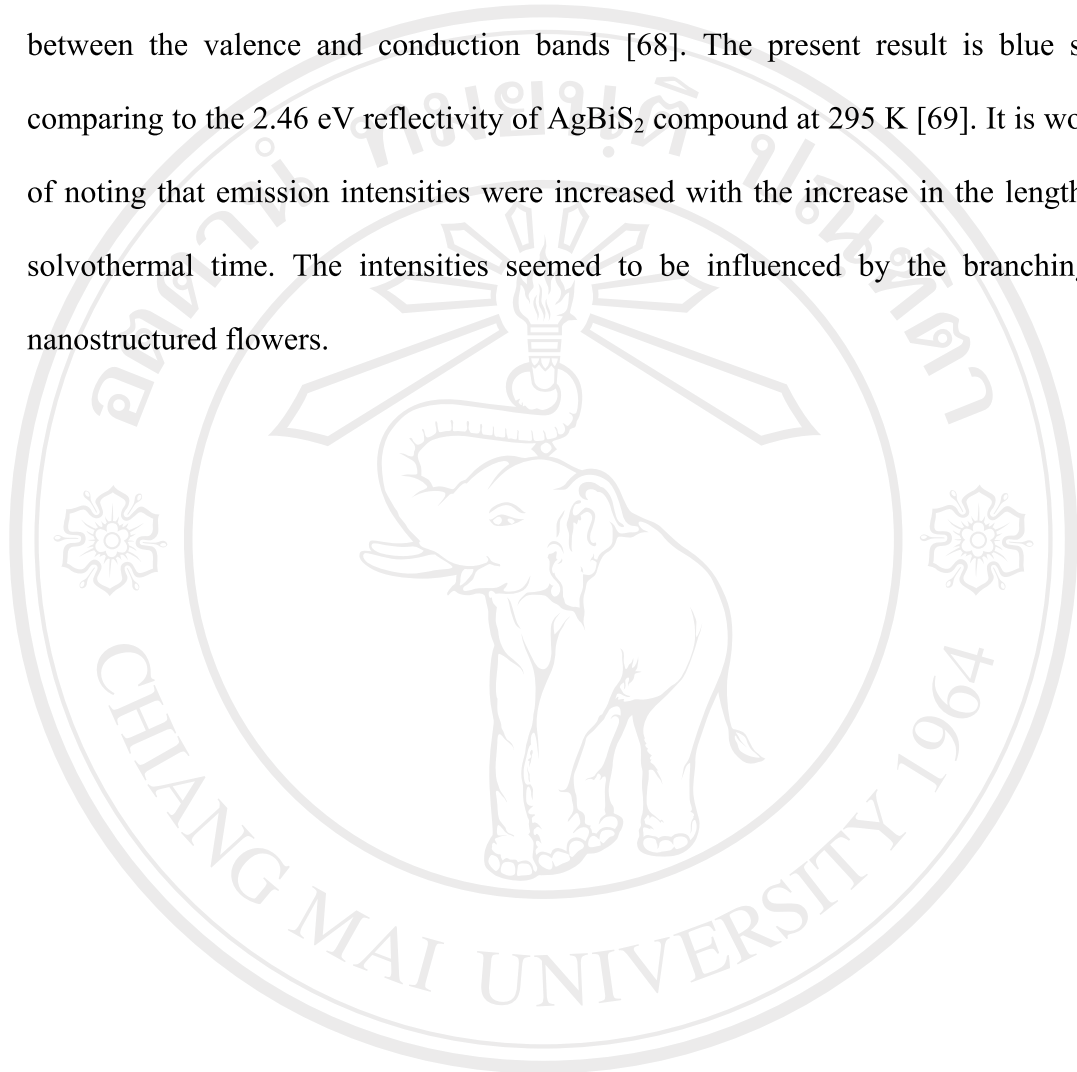


Figure 3.19 PL emissions of AgBiS_2 produced in EG at $200\text{ }^\circ\text{C}$ for 24 h - 72 h.

Photoluminescence (PL) emissions (Figure 3.19) of the products produced at $200\text{ }^\circ\text{C}$ solvothermal reaction for 24 h, 48h and 72 h were characterized using 200 nm excitation wavelength at room temperature. Their emission peaks were detected at the same wavelengths of 382 nm (3.24 eV) with surrounding shoulders. The emission peaks were caused by the recombination of electrons and electron holes (or holes) in trapped

surface states in the forbidden region [66,67], called energy band gap (or energy gap). But for the shoulders, they were caused by the shallow level of donors and acceptors between the valence and conduction bands [68]. The present result is blue shift, comparing to the 2.46 eV reflectivity of AgBiS₂ compound at 295 K [69]. It is worthy of noting that emission intensities were increased with the increase in the lengths of solvothermal time. The intensities seemed to be influenced by the branching of nanostructured flowers.



ลิขสิทธิ์มหาวิทยาลัยเชียงใหม่
Copyright© by Chiang Mai University
All rights reserved