

CHAPTER 2

EXPERIMENTAL PROCEDURE

2.1 Chemical reagents and equipments

2.1.1 Chemical reagents

- 1) Silver acetate, CH_3COOAg , $M_w = 166.93$, 99%, BDH Chem.
- 2) $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $M_w = 485.07$, 99%, Carlo Erba
- 3) Polyethylene glycol 200, PEG 200, $M_r = 190\text{-}200$, Fluka
- 4) Ethylene glycol, EG, $M_r = 62.070$, Carlo Erba
- 5) Propylene glycol, $\text{C}_3\text{H}_8\text{O}_2$, $M_r = 76.09$, >99%, Merck
- 6) Thiosemicarbazide, $\text{NH}_2\text{CSNHNH}_2$, $M_w = 91.13$, 99%, Acros
- 7) Deionized water
- 8) Ethanol, $\text{C}_2\text{H}_5\text{OH}$, 95%, Merck
- 9) Absolute ethanol, $\text{C}_2\text{H}_5\text{OH}$, 99.0-100.0% AR, Merck

2.1.2 Equipments

- 1) Hotplate and magnetic stirrer, model 502P-2, PMC Industries, Inc.,
San Diego, U.S.A.
- 2) Analytical balance, Model BP-210S, Satorius AG. Goettingen,
Germany
- 3) Oven, Model UE-400, Memmert, Germany
- 4) Ultrasonic bath, Bandelin Sonorex, Germany
- 5) X-ray Diffractometer, model D500/501, Siemens, Germany
- 6) Fourier Transform Infrared Spectrophotometer, FT-IR 510 Nicolet,
U.S.A.

- 7) Raman spectroscopy, model T64000 JY, Horiba Jobin Yvon, France
- 8) Perkin Elmer Luminescence spectrometer, model LS50B
- 9) Scanning Electron Microscope, model JSM-6335, JEOL, Japan
- 10) Transmission Electron Microscope, model JEM-2010, JEOL, Japan
- 11) Agate mortar

2.2 Synthesis of AgBiS₂ by solvothermal method

2.2.1 Effect of liquid media

CH₃COOAg, Bi(NO₃)₃.5H₂O and thiosemicarbazide (NH₂CSNHNH₂) were separately dissolved in different solvents [ethylene glycol (EG), water (H₂O), polyethylene glycol with molecularweight of 200 (PEG 200), and propylene glycol (PG)]. The Ag⁺ and Bi³⁺ solutions were mixed to form a mixture, to which the thiosemicarbazide solution was subsequently added. Volumes of each mixture were adjusted to be 50 ml, with 10 min stirring. The chemical reactions proceeded at 200 °C for 24 h, in tightly closed stainless steel autoclaves lined with Teflon. The precipitates were separated by filtering, washed with distilled water and 95 % ethanol, and dried in an oven at 70 °C for 24 h. The products were characterized to determine their phase (s), purity, morphologies and emissions.

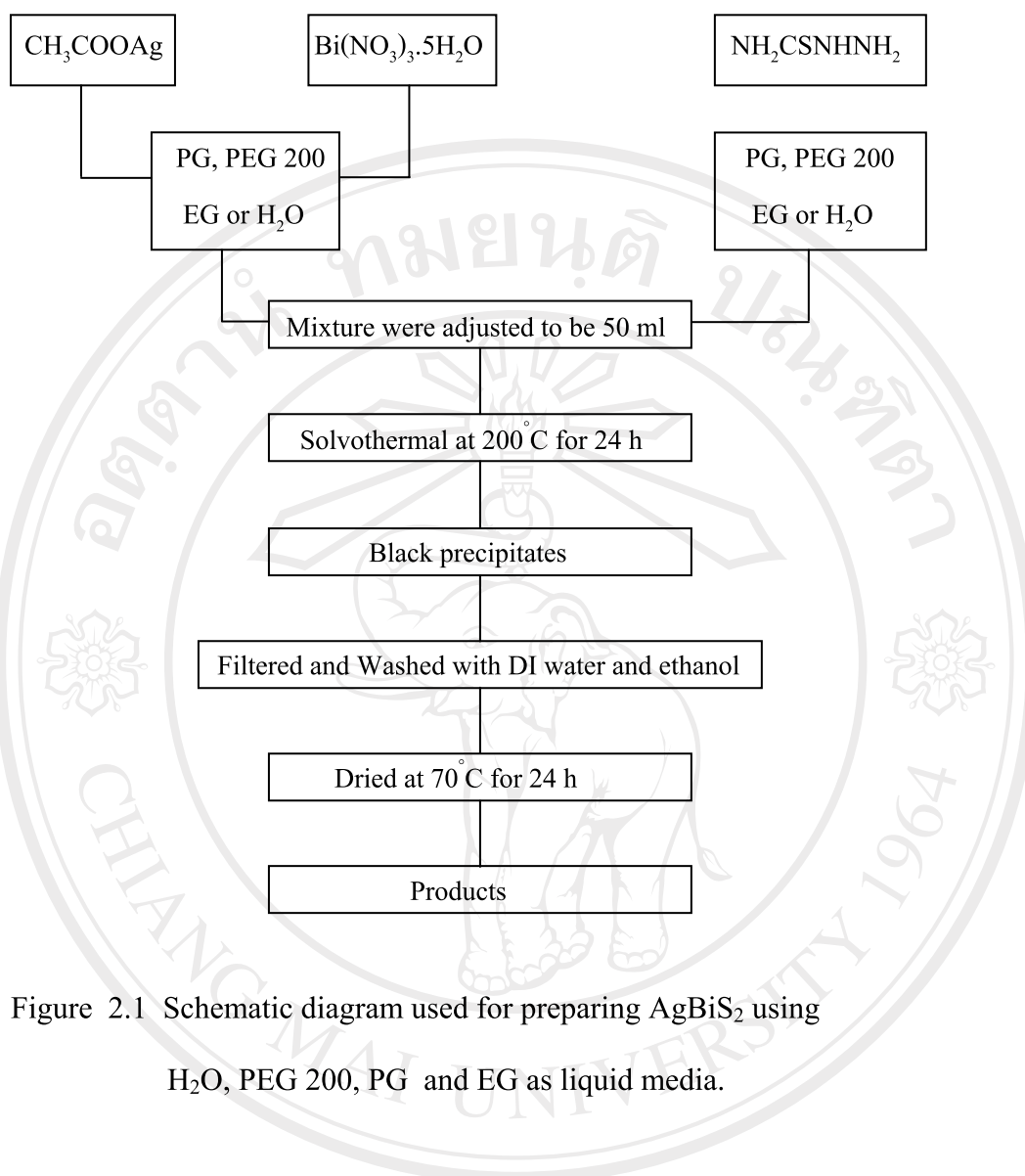


Figure 2.1 Schematic diagram used for preparing AgBiS_2 using H_2O , PEG 200, PG and EG as liquid media.

2.2.2 Effect of temperature

CH_3COOAg , $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and thiosemicarbazide ($\text{NH}_2\text{CSNHNH}_2$) were separately dissolved in ethylene glycol (EG). The Ag^+ and Bi^{3+} solutions were mixed to form a mixture, to which the thiosemicarbazide solution was subsequently added. Volumes of each mixture were adjusted to be 50 ml, with 10 min stirring. The chemical reactions proceeded at 140 °C, 160 °C, 180 °C and 200 °C for 24 h, in tightly closed stainless steel autoclaves lined with Teflon. The precipitates were

separated by filtering, washed with distilled water and 95 % ethanol, and dried in an oven at 70 °C for 24 h. The products were characterized to determine their phase (s), purity, morphologies and emissions.

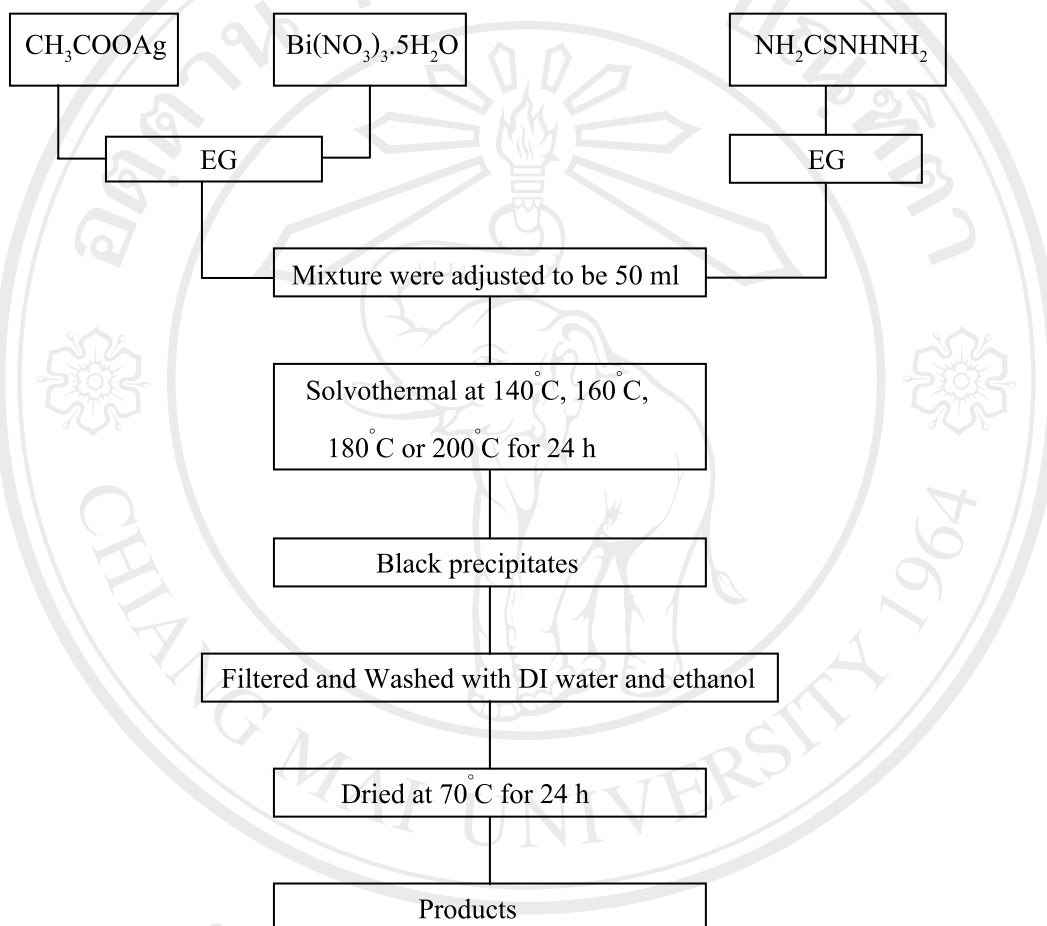


Figure 2.2 Schematic diagram used for preparing AgBiS_2 proceeded at 140 °C, 160 °C, 180 °C and 200 °C for 24 h

2.2.3 Effect of reaction time

CH_3COOAg , $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and thiosemicarbazide ($\text{NH}_2\text{CSNHNH}_2$)

were separately dissolved in ethylene glycol (EG). The Ag^+ and Bi^{3+} solutions were mixed to form a mixture, to which the thiosemicarbazide solution was subsequently added. Volumes of each mixture were adjusted to be 50 ml, with 10 min stirring. The

chemical reactions proceeded at 200 °C for 24 h, 48 h and 72 h, in tightly closed stainless steel autoclaves lined with Teflon. The precipitates were separated by filtering, washed with distilled water and 95 % ethanol, and dried in an oven at 70 °C for 24 h. The products were characterized to determine their phase (s), purity, morphologies and emissions.

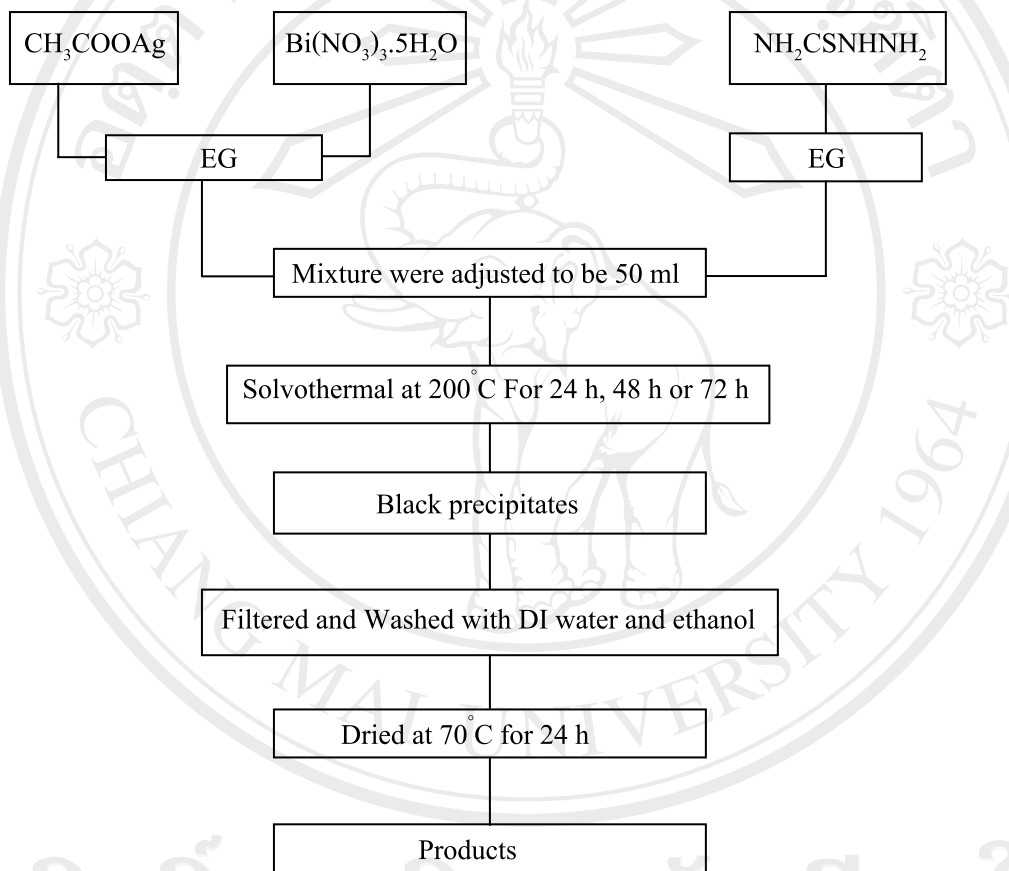


Figure 2.3 Schematic diagram used for preparing AgBiS₂ using different Reaction times.

2.3 Characterization

2.3.1 X-ray Diffraction (XRD)

The crystalline structure of product powders were characterized by X-ray diffractometry. The powder samples were finely grinded in agate mortar and then put on in sample holder. The crystallinity and phase purity of the products were analyzed by using X-ray diffractometry (XRD) with Cu K_{α} radiation ($\lambda = 1.5418 \text{ \AA}$) operating at 20 kV-15mA, at a scanning rate of $5^{\circ}/\text{min}$ in the 2θ range of 10° - 60° . The identification samples were assisted by Philips X'Pert Highscore Computer Software (search-match program) on the database of JCPDS software.



Figure 2.4 X-ray diffractometer

2.3.2 Scanning Electron Microscopy (SEM)

The morphologies of products were investigated using scanning electron microscopy. The powder samples were dispersed in absolute ethanol using an ultrasonic bath. The dispersed sample was dropped on conductive gold tape which attached to the SEM stub. The stub was then coated with gold particle in order to increase conductivity under argon atmosphere by plasma sputtering.

The morphology and particle sizes of as-obtained samples were determined by a Field emission-scanning electron microscope (SEM, JSM-6335F) operated at 15 kV accelerating voltage.



Figure 2.5 Scanning electron microscope

2.3.3 Transmission Electron Microscopy (TEM)

The morphology and electron diffraction of the samples were studied using transmission electron microscopy. The TEM samples were deposited on thin amorphous carbon films supported by copper grid from ultrasonically processed absolute ethanol solution of the sample powder.

The particle size and morphology was also observed by transmission electron microscope (TEM, JEOL JEM-2010) operating at 20 kV. The samples for TEM analysis were prepared by dispersing small amount of the powder in absolute ethanol and placing a drop of the solution onto a copper grid coated with holey carbon film and letting the ethanol evaporate slowly in air.



Figure 2.6 Transmission electron microscope

2.3.4 Photoluminescence Spectroscopy

Optical properties of the products were analyzed by photoluminescence spectroscopy. The appropriated amount of powder samples were dispersed in absolute ethanol using ultrasonic bath. Photoluminescence (PL) spectrometer was operated using a 200 nm exciting wavelength for AgBiS₂.

The luminescence emission spectra of the samples were investigated using Perkin Elmer Luminescence spectrometer LS50B at room temperature.

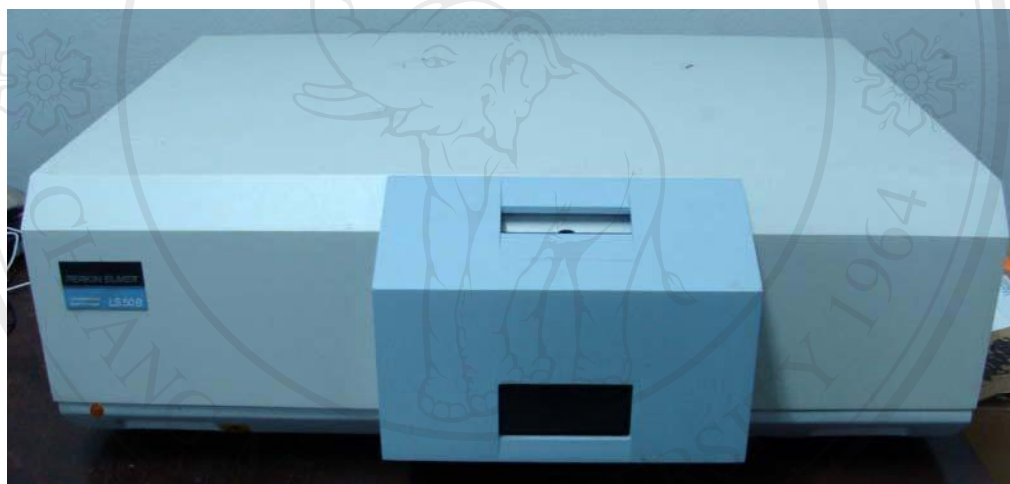


Figure 2.7 Luminescence spectrometer