

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Synthesis of CuInSnO_4 by Sol-Gel Method

After preparation the mixed metal mixture by sol-gel method, the color of metal mixture solution was transparent dark blue. No colloidal dispersion was appeared, obtaining a homogeneous solution, due to diethanolamine acting as a directing agent to form hydroxyl bond or oxo bond with the precursor in the sol-gel process, resulting in network formation, as indicated by *Traversa et al., 2001* and *Verma et al., 2007*.

4.2 Synthesis of CuInSnO_4 Nanofibers via Electrospinning Method

Pure PVA solution was first used to find a suitable viscosity for achieving smooth fibers. The optimal conditions found were to use 10% of PVA at 15 cm distance and 12 kV voltage to obtain continuous fibers with nano-scale size although some beads occurred and the fibers merged together (Figure 4.1).

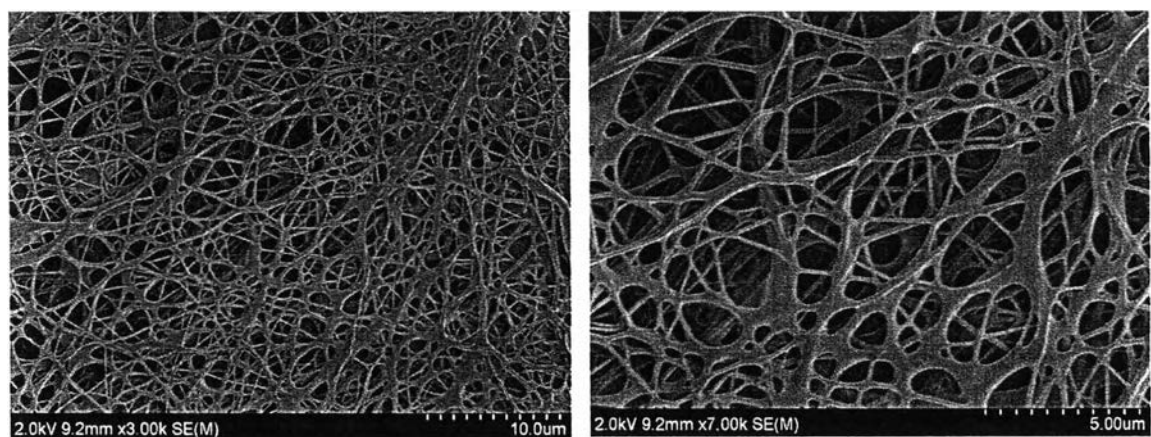


Figure 4.1 Micrographs of 10% PVA spun at 15 cm distance and 12kV, and taken with magnification of A) 3,000x and B) 7,000x.

These spinning conditions were further used to mix with the mixed metal solution, by mixing the metal mixture with 10% of PVA (1:10 by volume) and stirring for 30 min to obtain homogeneous solution before spinning. The mixture was electrospun by varying the distance between the charge and the needle (15, 17, and 20 cm) and the voltage of the electric field (12, 15, and 16 kV).

Effect of distance

Metal mixture solution was spun at various distances between the charge and the needle (15, 17, and 20 cm) with the same voltage of 15 kV. The SEM results showed different fiber morphologies. At the distance of 15 cm, a large amount of beads were obtained and there were no continuous fibers. Similar to the distance of 17 cm, fibers were not continuous either, but a smaller amount of beads were seen. The 20 cm distance gave continuous fibers and much less beads (Figure 4.2). According to *Supaphol et al., 2008*, an increase in the collection distance caused the electrostatic field strength (EFS) to decrease. The decreased EFS caused both the electrostatic and the Coulombic repulsion forces to decrease, resulting in the decrease of the droplet formation. Moreover, the increase of the collection distance also resulted in the formation of smooth fibers without the presence of beads, indicating that the jet was stretched enough prior to the deposition on the collector.

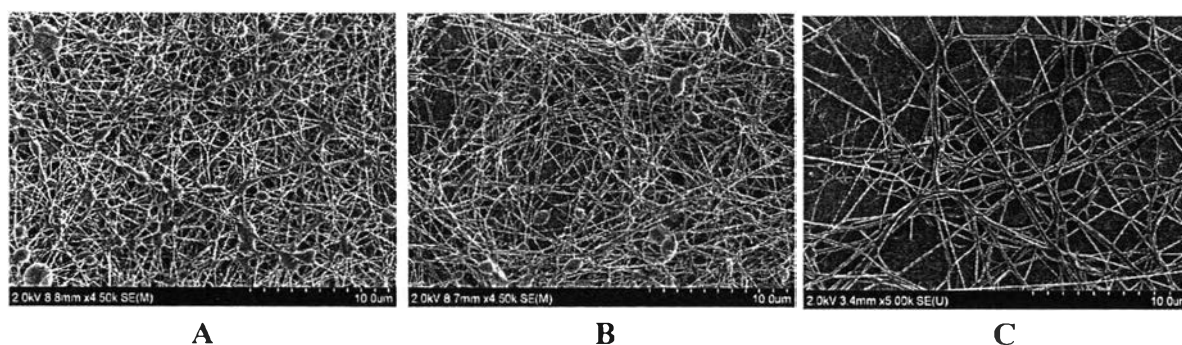


Figure 4.2 SEM images of mixed metal mixture spun at 15 kV, and various distances; A) 15 cm, 4500x, B) 17 cm, 4500x, and C) 20 cm, 5,000x.

Effect of voltage

By fixing the distance at 20 cm the voltage was varied (12, 15, and 16 kV) to study its effect on the fiber formation. The SEM results gave different fiber morphologies. At 12 kV, many beads formation were found and the fibers were neither continuous nor smooth, while 15 kV still gave some beads, but the fibers were smoother. The 16 kV seemed to be the best since it gave continuous and smooth fibers and small amount of beads. It means, the increase of the voltage also decreased the size of the beads and the fiber shape to be more elongated (Figure 4.3).

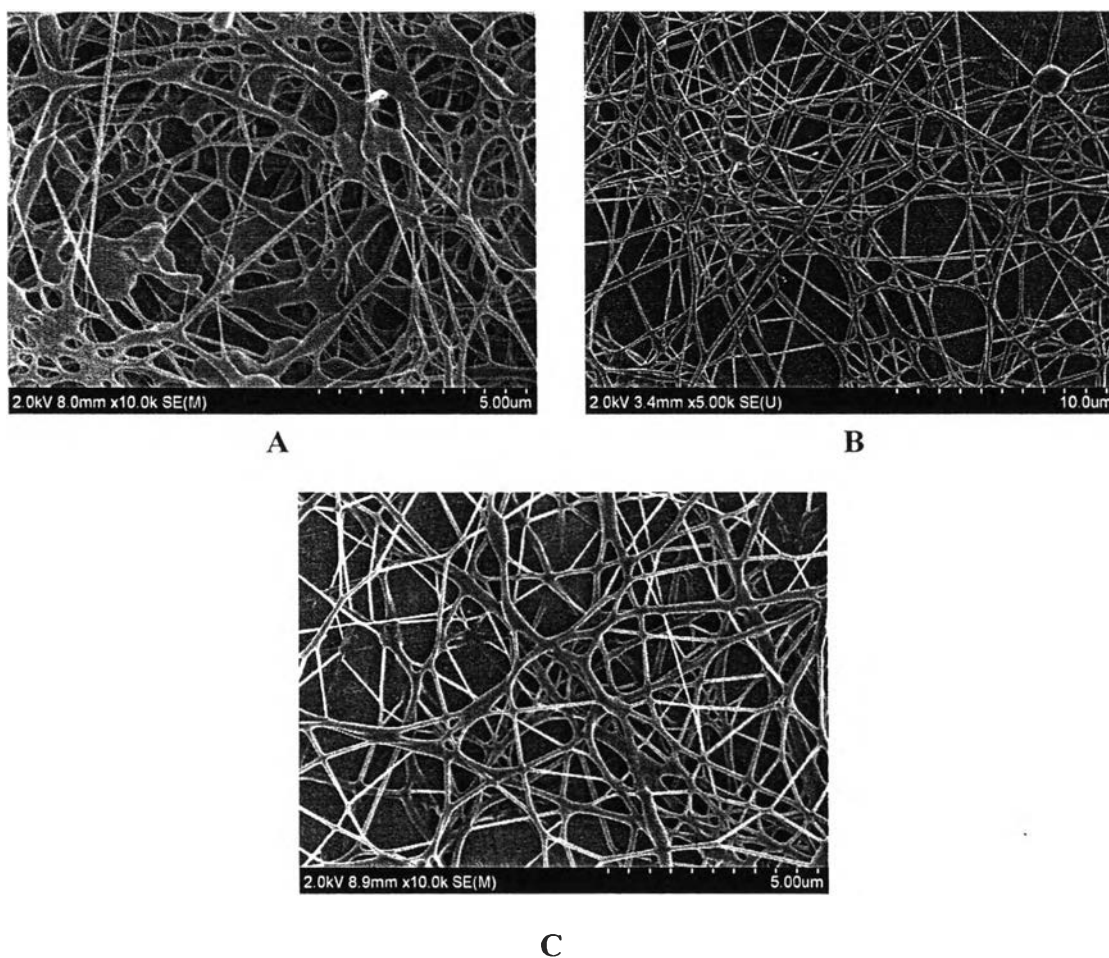


Figure 4.3 SEM images of mixed metal mixture spun at 20 cm distance and various voltages; A) 12 kV, 10,000x, B) 15 kV, 5,000x, C) 16 kV, 10,000x.

It was found that the fibers spun at 20 cm distance and 16 kV voltage provided small amount of beads and gave continuous fibers when comparing with other conditions (Figures 4.4 – 4.6). The reason is that at higher distance and high voltage, fibers injected from syringe were dried completely and dispersed throughout the aluminium foil and the charge due to metal ion caused the bead formation decrease, as studied by *Supaphol et al., 2008*.

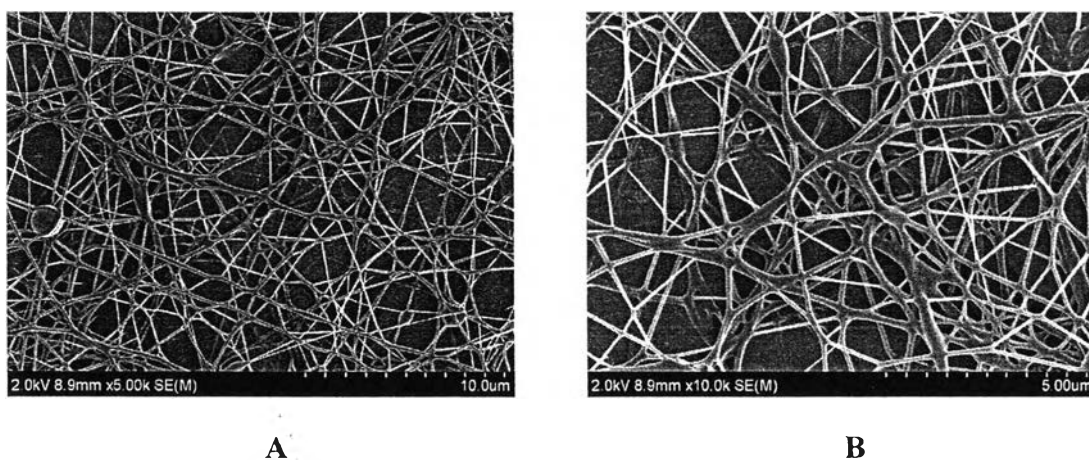


Figure 4.4 SEM images of mixed metal mixture spun at 20 cm distance and 16 kV;
A) 5,000x and B) 10,000x.

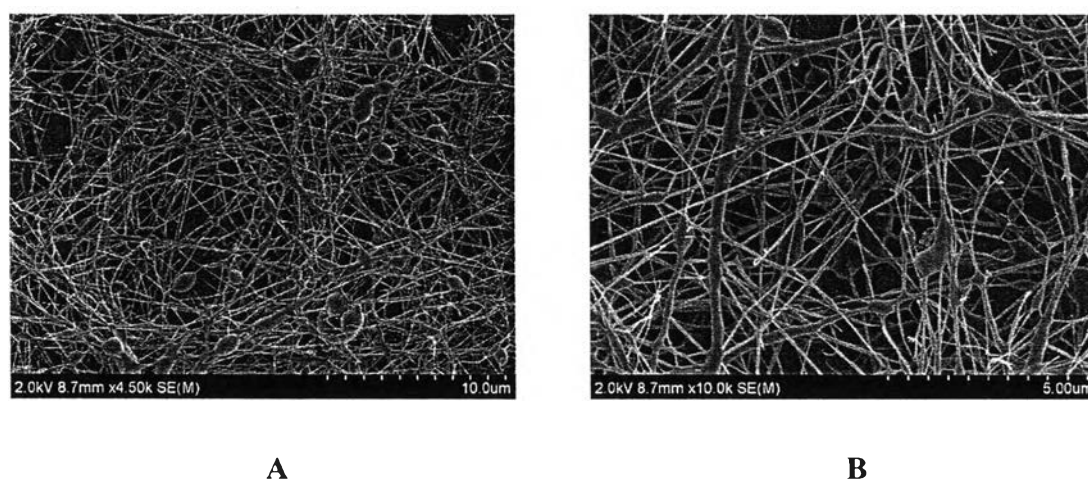


Figure 4.5 SEM images of mixed metal mixture spun at 17 cm distance and 15 kV;
A) 4,500x and B) 10,000x.

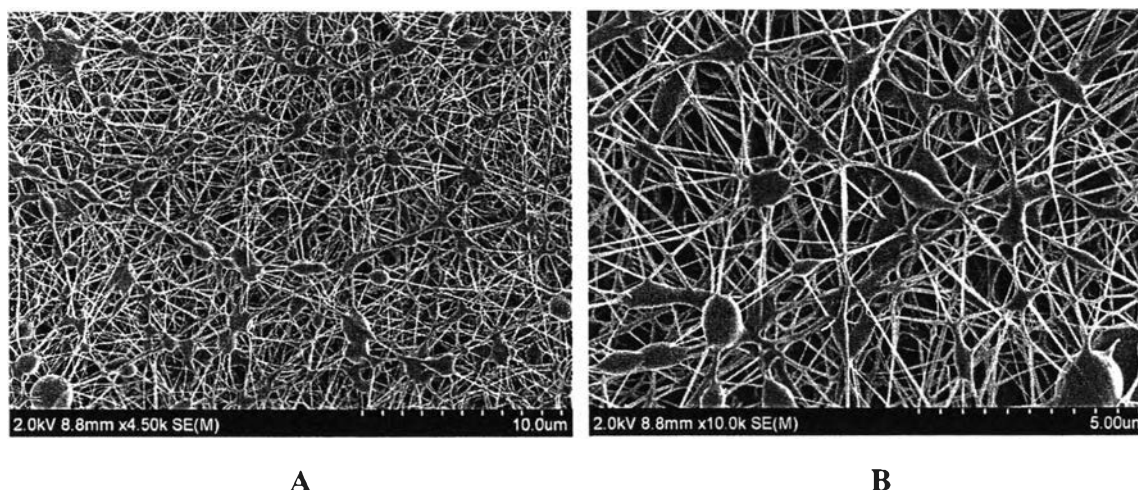


Figure 4.6 SEM images of mixed metal mixture spun at 15 cm distance and 15 kV; A) 4,500x and B) 10,000x.

After electrospinning process, the fibers were calcined at 800°, 900°, 950°, and 1100 °C at a rate of 0.5 °C per min to eliminate PVA and any organic components to form mixed metal oxide products (Figures 4.7 – 4.8). When increasing temperature, the fibers were collapsed and agglomerated. The reasons could be following; 1) using too small amount of metal mixture in large amount of PVA, thus after calcinations to eliminate PVA, there was too small amount of metal oxide to form fibers; 2) no formation of the oxo or hydroxo bonds between each metal before spinning due to too short stirring time (*Supaphol et al., 2008*); and 3) using too high heating rate, as studied by Zhang et al., 2009, who calcined fibers at 700 °C for 18 h, using a decreasing heating rate from 5 °C per min to 2 °C per min to obtain a good fiber structure. When PVA and any organic components were eliminated, the as-prepared product became particles instead of fibers (Figures 4.9). Therefore, the conditions were adjusted by using larger amount of metal mixture (0.3 to 1 mL), increasing the stirring time before spinning for the formation of the oxo or hydroxo bonds between each metal (from 15 min to 24 h), also decreasing the heating rate (from 1 °C to 0.3 °C per min). From the SEM results in Figure 4.10, the precursors/PVA fibers calcined at 950 °C using the heating rate of 0.3 °C per min provided mixed metal oxide fibers.

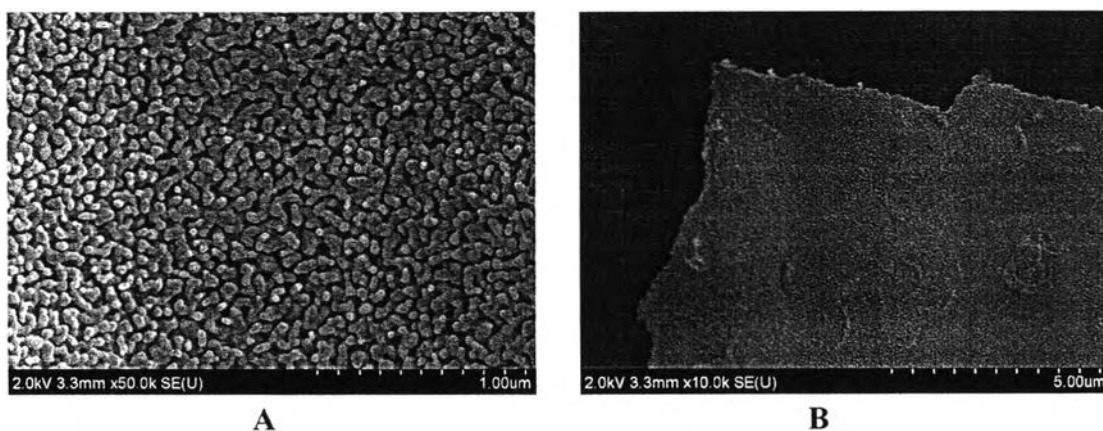


Figure 4.7 SEM images of mixed metal mixture spun at 20 cm distance, 16 kV, calcined at 800 °C heating rate 0.5 °C/m; A) 50,000x and B) 10,000x.

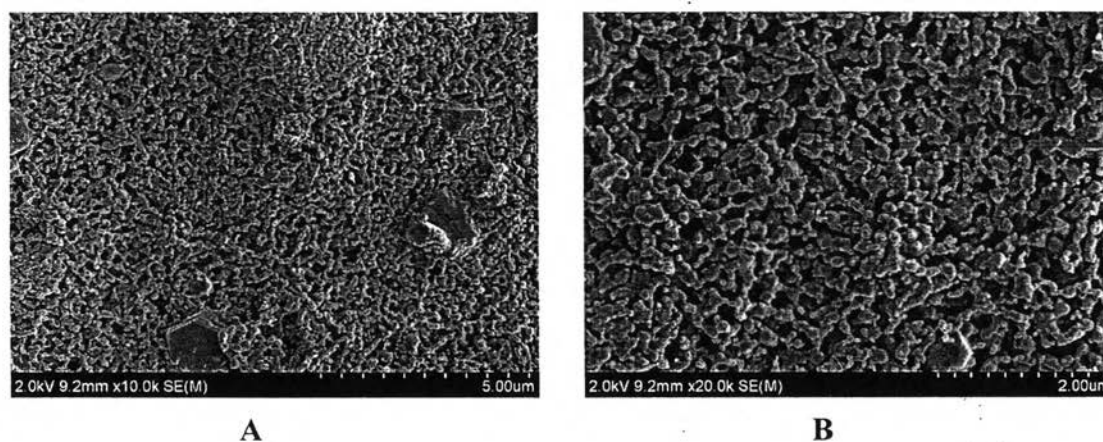


Figure 4.8 SEM images of mixed metal mixture spun at 20 cm distance, 16 kV, calcined at 900 °C heating rate 0.5 °C/m; A) 10,000x and B) 20,000x.

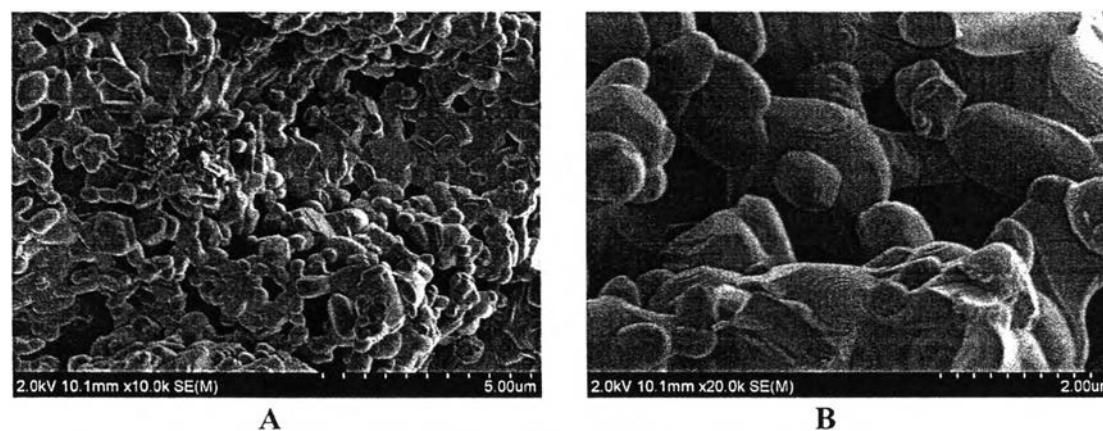


Figure 4.9 SEM images of mixed metal mixture spun at 20 cm distance, 16 kV, calcined at 1,100 °C heating rate 0.5 °C/m; A) 10,000x and B) 20,000x.

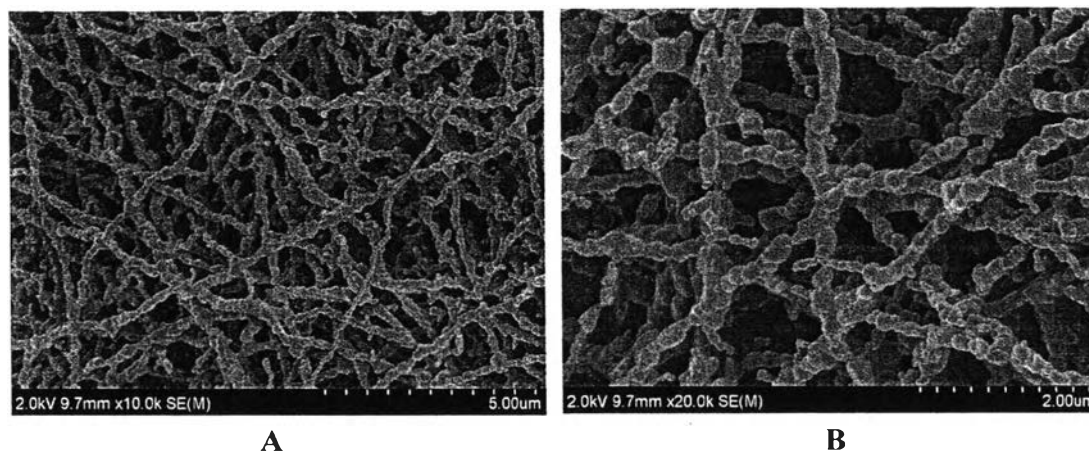


Figure 4.10 SEM images of mixed metal mixture spun at 20 cm distance, 16 kV, calcined at 950 °C with a 0.3°C per min heating rate; A) 10,000x and B) 20,000x.

The XRD results of the product calcined at 800 °C and showing mixed phases of indium oxide (In_2O_3), tin oxide (SnO_2) and very small amount of copper oxide (CuO) could confirm the SEM result that the collapsed and merged fibers occurred, probably due to non-homogeneity of the mixed metal solution before spinning. Moreover, in this case, the calcinations temperature at 800 °C was too low to form spinel structure, as studied by Ingram *et al.* who synthesize CdInSnO_4 by solid-state method and obtained the spinel structure, at 1175 °C. In our case, the products were calcined at various heating temperatures, including 900°, 950°, and 1100 °C, higher than 800 °C, at a heating rate of 0.5 °C per min (Figure 4.11), and the results looked like containing the mixed phases of indium oxide (In_2O_3), tin oxide (SnO_2) and copper oxide (CuO). However, this CuInSnO_4 is a new compound and no one has ever synthesized, thus, the phases showing could be belong to either those three metal oxides or pure spinel phase product, or both overlapping each other.

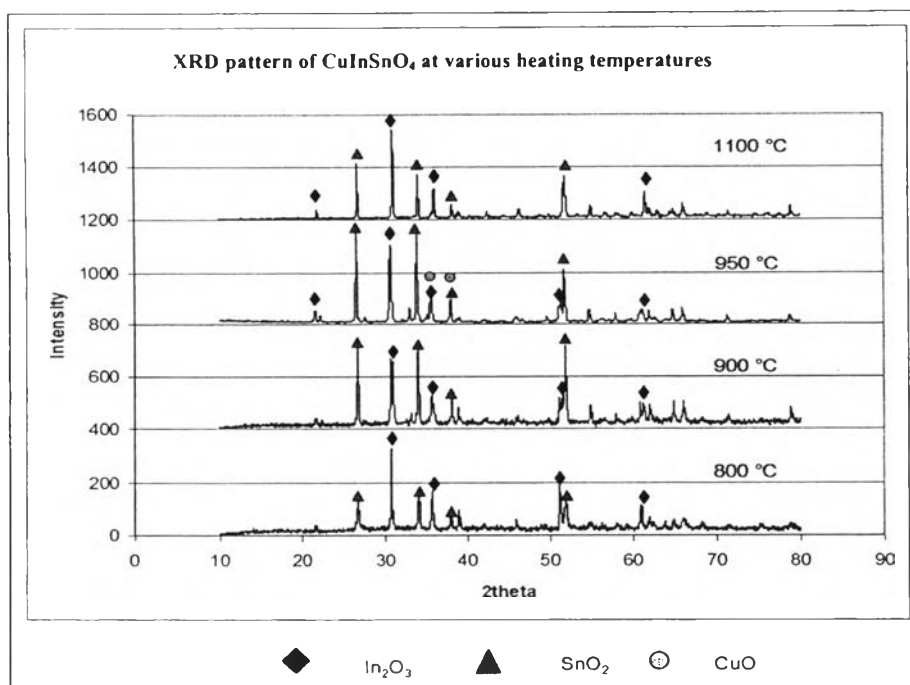


Figure 4.11 XRD patterns of CuInSnO₄ at various heating temperatures for 36 h with the heating rate of 0.5 °C per min.

In addition, the synthesized mixed metal oxide fibers were compared peaks with other XRD patterns of spinel structure phase, including MgAl₂O₄ (Kong *et al.*, 2002), Fe₃O₄ (Kaczmarek *et al.*, 1997), NiAl₂O₄ (Hasin *et al.*, 2007), and CuInSnO₄ (Dedryve`re *et al.*, 2000), by using Bragg's Law equation (Eq. 4.1-4.2), and the results are shown in Table 4.1. According to the calculation, the XRD pattern of the spinel structure phase of each compound provides the similar unit cell parameter (*a*) for different 2Thetas. The spinel structure phase shows peaks at the same hkl plane for different d-spacings or different 2Theta positions. Therefore, the XRD results of the synthesized mixed metal oxide compound (CuInSnO₄) showed the mixed phases of the spinel structure and other oxide phases, including indium oxide (In₂O₃), tin oxide (SnO₂), and copper oxide (CuO), (Figure 4.12).

$$n\lambda = 2d\sin\theta. \quad (\text{Eq. 4.1})$$

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad (\text{Eq. 4.2})$$

Table 4.1 The spinel structure phase pattern of various spinel structure compounds

| Compound | 2Theta | d-spacing (Å) | hkl plane | Intensity % | Unit cell parameter (a) (Å) |
|--|--------|---------------|-----------|-------------|-----------------------------|
| MgAl ₂ O ₄ | 31.50 | 2.837 | 220 | 45 | 8.0279 |
| | 37.50 | 2.396 | 311 | 100 | 7.9373 |
| | 39.00 | 2.307 | 222 | 5 | 7.9784 |
| | 45.00 | 2.013 | 400 | 50 | 8.0436 |
| | 63.25 | 1.469 | 440 | 45 | 8.3066 |
| Fe ₃ O ₄ | 22.00 | 4.036 | 111 | 20 | 6.9857 |
| | 36.00 | 2.492 | 220 | 40 | 7.0490 |
| | 42.00 | 2.149 | 311 | 100 | 7.1277 |
| | 51.00 | 1.789 | 400 | 38 | 7.1554 |
| | 75.50 | 1.265 | 440 | 43 | 7.1186 |
| NiAl ₂ O ₄ | 37.50 | 2.396 | 311 | 100 | 7.9435 |
| | 45.00 | 2.013 | 400 | 55 | 8.0436 |
| | 66.00 | 1.414 | 440 | 60 | 7.9974 |
| CuInSnS ₄ | 15.00 | 5.900 | 111 | 60 | 10.2176 |
| | 24.00 | 3.704 | 220 | 20 | 10.4737 |
| | 27.50 | 3.241 | 311 | 100 | 10.7424 |
| | 29.50 | 3.024 | 222 | 20 | 10.4761 |
| | 34.00 | 2.634 | 400 | 60 | 10.5309 |
| | 49.50 | 1.839 | 440 | 60 | 10.5033 |
| The mixed metal oxide compound (CuInSnO ₄) | 22.20 | 4.000 | 220 | 20 | 11.3090 |
| | 26.56 | 3.352 | 311 | 100 | 11.1120 |
| | 27.56 | 3.234 | 222 | 15 | 11.1980 |
| | 33.06 | 2.707 | 400 | 40 | 10.8258 |
| | 51.32 | 1.778 | 440 | 30 | 10.0593 |

However, there are researches involving in the effect of calcination temperature on the spinel structure phase formation (*Hongyu et al., 2004, Ingram et al., 2004, Dedryve`re et al., 2000*). The fibers were also calcined at 950 °C for 36 h using 0.3 °C per min heating rate and the XRD result was similar to that calcined at the same conditions, except using the heating rate of 0.5 °C per min (Figure 4.12). The obtained mixed metal oxide fibers provided higher surface area of 60 m²/g than non-fibers, 6 m²/g that were showed in Table 4.2.

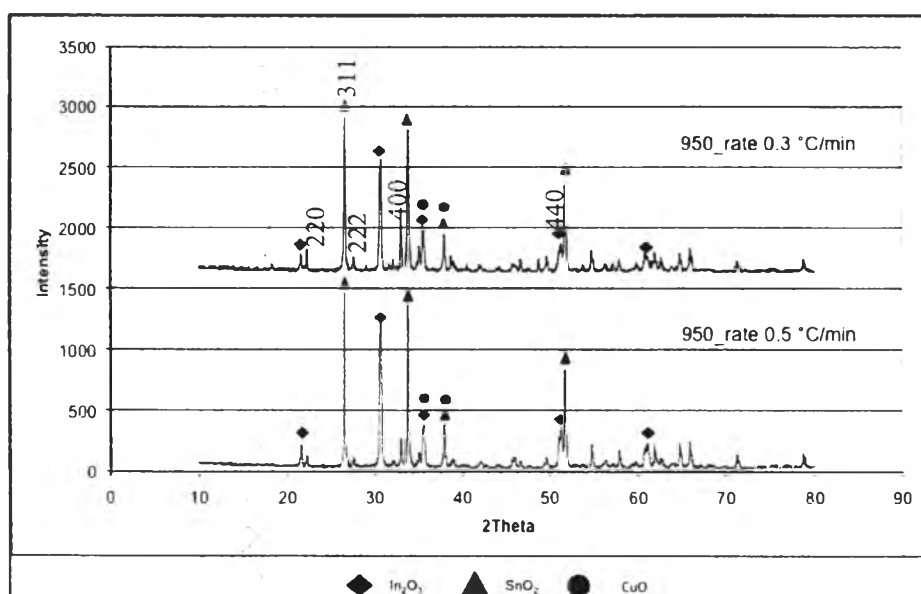


Figure 4.12 XRD patterns of CuInSnO₄ at 950 °C for 36 h with the heating rates of 0.5 and 0.3 °C per min.

Table 4.2 Surface area, pore volume, and pore size of fiber and non-fiber product of CuInSnO₄

| Type of Product | Surface Area (m ² /g) | Total Pore Volume (cc/g) | Average Pore Diameter (nm) |
|-----------------|----------------------------------|--------------------------|----------------------------|
| Fibers | 60.49 | 0.07 | 3.10 |
| Non-fibers | 6.43 | 0.02 | 11.04 |

Furthermore, the mixed metal oxide fibers at various calcination temperatures were measured conductivity using LCR meter adjusted the frequency and the voltage at 50 Hz and 4.0 V, respectively, the same as the conditions used in a typical Li-ion battery. The results showed that fibers calcined at high temperature increased resistivity. The reason could be that an increase in calcination temperature might eliminate the free electrons that enhance conductivity of the mixed metal oxide compounds (Table 4.3) (Cheng J.G. *et al.*, 2003 and Soliman S.A. *et al.*, 2009).

Table 4.3 Conductivity data of mixed metal oxide compound fibers at various calcination temperatures

| Calcination temperature (°C) | Resistivity (k Ω) | Conductivity (kS) |
|------------------------------|---------------------------|-------------------|
| 800 | 1.3387 | 0.7469 |
| 900 | 5.3572 | 0.1866 |
| 950 | 8.2357 | 0.1214 |
| 1100 | 89.8436 | 0.0111 |