

# CuFeO<sub>2</sub> formation using fused deposition modeling 3D printing and sintering technique

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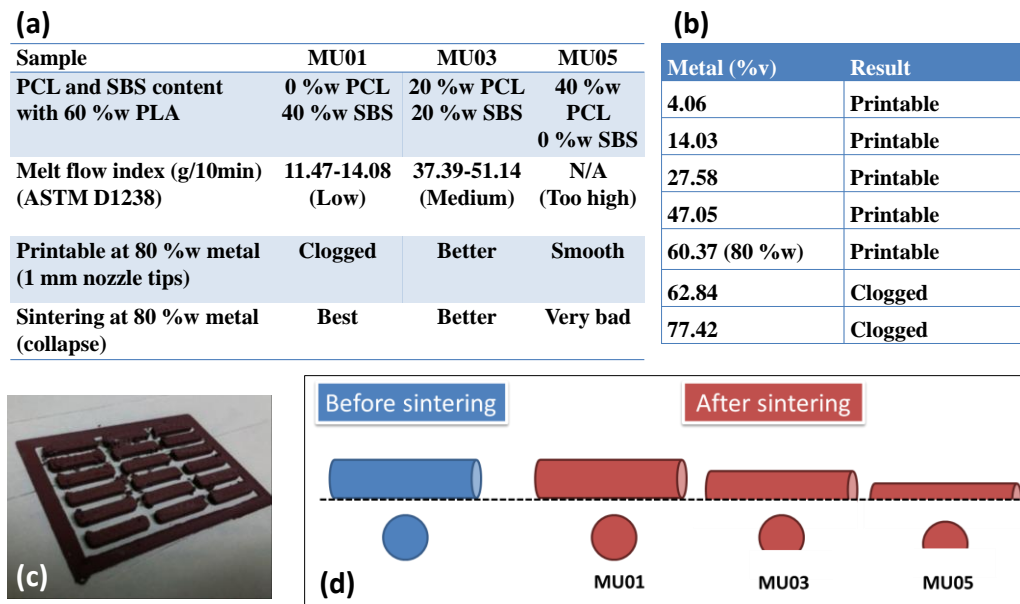
**Abstract.** CuFeO<sub>2</sub> is a metal oxide mineral material which is called delafossite. It can potentially be used as a chemical catalyst, and gas sensing material. There are methods to fabricate CuFeO<sub>2</sub> such as chemical synthesis, sintering, sputtering, and chemical vapor deposition. In our work, CuFeO<sub>2</sub> is prepared by Fused Deposition Modeling (FDM) 3D printing. The composite filament which composed of Cu and Fe elements is printed in three dimensions, and then sintered and annealed at high temperature to obtain CuFeO<sub>2</sub>. Suitable polymer blend and maximum percent volume of metal powder are studied. When percent volume of metal powder is increased, melt flow rate of polymer blend is also increased. The most suitable printing condition is reported and the properties of CuFeO<sub>2</sub> are observed by Scanning Electron Microscopy, and Dynamic Scanning Calorimeter, X-ray diffraction. As a new method to produce semiconductor, this technique has a potential to allow any scientist or students to design and print a catalyst or sensing material by the most conventional 3D printing machine which is commonly used around the world.

## 1. Introduction

Copper iron oxide (CuFeO<sub>2</sub>) or delafossite is oxides type of copper that first discovered by Friedel and Hebd [1] in 1873. The potential applications of CuFeO<sub>2</sub> compound has been studied such as antimicrobial, catalyst and batteries semiconductor [2-4] due to its optical, magnetic, and electrical properties. CuFeO<sub>2</sub> have many fabrication methods such as sol-gel or solid state reactions [4, 5]. The CuFeO<sub>2</sub> have never fabricated by new technique like 3D printing. The 3D printing as a new era in manufacturing has widely used in industry and laboratory especially Fused Deposition Modeling (FDM) 3D technique [6]. The FDM usually use polymer filament or composite filament which is later on melted on a platform to get 3D object. The advanced 3D filament has fabricated in laboratory as a high loading additive composite such as 50 %w BaTiO<sub>3</sub> filament however the amount of additive was still limited [7]. In this study, A mixture between Cu and Fe powder was blended with a suitable polymer and reported as a first CuFeO<sub>2</sub> preparation by FDM printing technique and sintering process. The CuFeO<sub>2</sub> can be easily designed to be a simple or a complicated structure by any researcher.

## 2. Experiments

Polylactic acid (PLA), Styrene-butadiene-styrene (SBS) and Polycaprolactone (PCL) were mixed with copper (Cu) - iron (Fe) powder with weight ratio of 20:80 to obtain CuFe-blend. The Cu-Fe powder is 1:1 atomic ratio. The CuFe-blend filament was fabricated by extrusion technique at 220 °C with 14 mN/m<sup>2</sup> to get 1.75 mm filament diameter. The size is standard size for FDM 3D printing



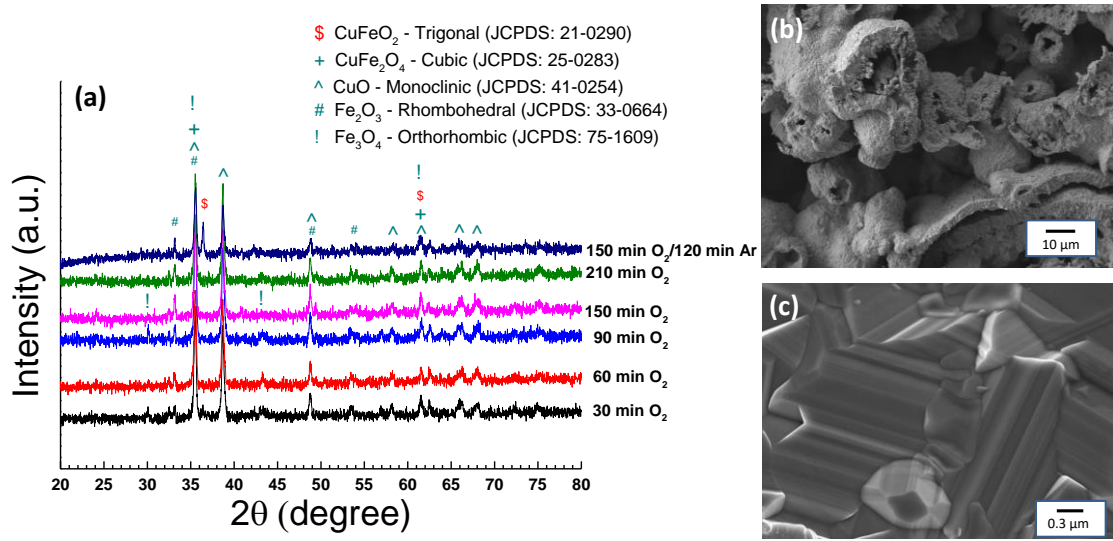
**Figure 1.** (a) Polymer content and MFI value of MU01, MU03 and MU05, (b) maximum metal content of MU03 with 1 mm nozzle tips, (c) CuFe-blend sample after printing and (d) sample collapsed after sintering of MU01, MU03 and MU05 with 80% w metal.

machine. Then, the filament was printed and sintered in furnace at 700 °C under 1 atm O<sub>2</sub> and Ar gas flow respectively to obtain CuFeO<sub>2</sub> complex. The gas flow rate was constant at  $5 \times 10^{-4}$  m<sup>3</sup>/s with same volume of sample. Moreover, the CuFeO<sub>2</sub> complex was confirmed phase structure and observed structure by X-ray diffraction (XRD) and Scanning Electron Microscope (SEM). XRD pattern had used JCPDS no. 21-0290, 25-0283, 41-0254, 33-0664, 75-1609 as referred to CuFeO<sub>2</sub> phase, CuFe<sub>2</sub>O<sub>4</sub> phase, CuO phase, Fe<sub>2</sub>O<sub>3</sub> phase and Fe<sub>3</sub>O<sub>4</sub> phase, respectively. Differential Scanning Calorimetry (DSC) and Thermo Gravimetric Analysis (TGA) were used to analyse weight loss of the sample and phase transformation under gas flow with 10°C/min rate. Moreover, polymer blend were observed with melt flow indices (MFI) by melt flow indexer (KAYENESS) according to ASTM D1238 with load 2.1 kg, 170 °C that temperature is near operated FDM temperature.

### 3. Results and discussion.

#### 3.1. Printing condition

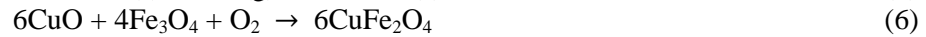
Polymer blend were examined viscosity by MFI test. Moreover, CuFe-blend filaments were examined clogged nozzle tip and collapsed sample by printing and sintering testing as showed in figure 1a. PLA of 60 %w polymer blend were shown with different PCL and SBS polymer content as shown in figure 1a. MU01, MU03 and MU05 are made up of of 40 %w SBS without PCL, 20 %w SBS with 20 %w PCL, and 40 %w PCL without SBS, respectively. SBS have molecular weight (MW) higher than PCL, so the MU01 had low MFI or high viscosity [8, 9]. Finally, MU01 was much easier to clog with 80%w metal around nozzle tip because MFI are related to MW distributions of polymer [10]. In contrast, MU05 was much easier to smooth printable but MU05 blend with metal was easy collapsed because of too high MFI as showed in figure 1d. MU03 was better collapsed sample, so MU03 was the best choice for use in this case. Moreover, MU03 was mixed and blended with 4.06 - 77.42 %v metal powder as showed in figure 1b. From 4.06 to 60.37 %v metal powder, those had smooth flow printable at nozzle tip as shown printed sample in figure 1c until metal powder of 62.84 %v had clogged tip. In the suitable polymer blend and metal powder content, MU03 and 60.37 %v are the best condition for use in this case because that are smooth flow of printable and good sintering process.



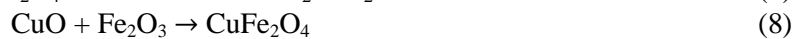
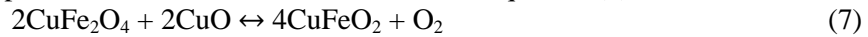
**Figure 2.** (a) XRD patterns of sample prepared by five duration time technique are 30, 60, 90, 150 and 210 min with O<sub>2</sub> flow, and the best condition to obtain CuFeO<sub>2</sub> phases at 150 and 120 min duration time with O<sub>2</sub> and Ar flow respectively; Morphology internal area inside the CuFeO<sub>2</sub> complex at different magnifications (b) low magnification and (c) high magnification.

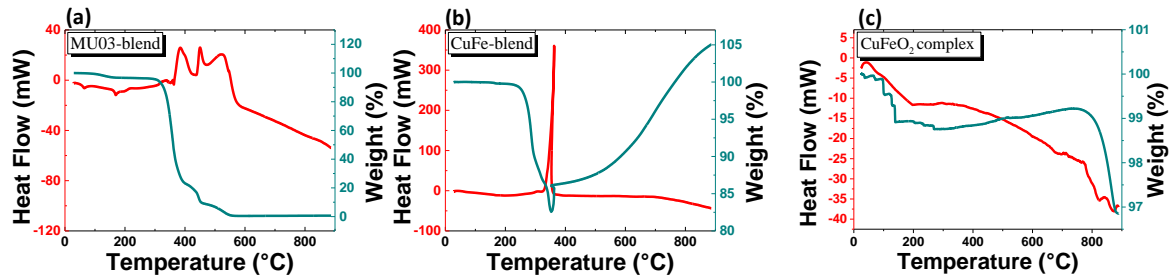
### 3.2. XRD characterization of the synthesis composites.

To grow CuFeO<sub>2</sub>, Cu-Fe blend were calcined and sintered in furnace which divided by two steps of O<sub>2</sub> and Ar gas experiments. The first step, CuFe-blend was sintered in O<sub>2</sub> gas for 30-210 min duration time to find the strongest peak with sufficient duration time. An XRD pattern was shown copper-iron oxide phases in figure 2a. At 62° peak, it was showed that 30 minute duration time has the weakest peak whereas 150 and 210 minute duration times have the strongest peak. That peak might be CuO or CuFe<sub>2</sub>O<sub>4</sub> phases which phases are necessary to obtain CuFeO<sub>2</sub> as well. Therefore, 150 minute is adequate amount of duration time in the first step. In transformation mechanism, it might be suggested that Cu powders were transformed to CuO easily than Cu<sub>2</sub>O followed by equation (1)-(3) [11]. Moreover, Fe powders were transformed to Fe<sub>2</sub>O<sub>3</sub> with Fe<sub>3</sub>O<sub>4</sub> but the Fe<sub>3</sub>O<sub>4</sub> powder was easily transformed than Fe<sub>2</sub>O<sub>3</sub> because of lower enthalpy energy (DH°) following equation (4) and (5). Afterward, CuO and Fe<sub>3</sub>O<sub>4</sub> were formed to CuFe<sub>2</sub>O<sub>4</sub> at inter-particle followed by equation (6). In the first step mechanism, it could be the case that Cu and Fe particles are good inter-particle diffusion sintering before Cu and Fe are transformed to be oxide of Cu and Fe respectively.



The second step, the sample of 150 minute duration time O<sub>2</sub> gas was calcined continuously in Ar gas with 120 minute duration time as showed in figure 2a. The CuFeO<sub>2</sub> phases clearly appeared at 36.4° peak. It could be that phase was transformed only at the inter-particle (poor contact) because surface energy is transformed easily. So, CuFeO<sub>2</sub> intensity hasn't strong and other oxide phases still remains peak. In transformation mechanism, it not only is inert gas non-interaction with particle, but also it can help to be more stable phases. While calcining condition, both CuO and CuFe<sub>2</sub>O<sub>4</sub> at inter-particle were transformed to CuFeO<sub>2</sub> phase as shown in equation (7) [12, 13]. Moreover, CuFe<sub>2</sub>O<sub>4</sub> can be formed as well at inter-particle of CuO and Fe<sub>2</sub>O<sub>3</sub> as showed in equation (8) [11].





**Figure 3.** (a) DSC and TGA of MU03-blend, (b) DSC and TGA of CuFe-blend and (c) DSC and TGA of CuFeO<sub>2</sub> complex in inert gas.

### 3.3. Morphology and inter-particle of CuFeO<sub>2</sub> complex.

As shown in figure 2b and c, the cross-section of CuFeO<sub>2</sub> complex sample were observed inter-particle and grain boundary by SEM with different magnification. The sample inside was scaffold that has several porous structure as reported [14]. While sintering process, the pore was occurred several inside the sample because of decomposed polymer blend. The particles were irregular shape that leads to be weak agglomeration and low mechanical properties [14]. The particles have good inter-particle diffusion sintering, so metal oxide was formed and led to CuFeO<sub>2</sub> formation at particle interface. In terms of average grain size effects, many papers were reported that such as average grain size was increased with increasing duration time and air flow rate [15]. At short duration time, the inter-particle diffusion was shorted, and then average grain size must be smaller.

### 3.4. Phase transformation of CuFe-blend and CuFeO<sub>2</sub> complex.

DSC/TGA had been used to investigate the phase transformation of CuFe-blend and CuFeO<sub>2</sub> material, which heat up at room temperature to 900 °C with 10 °C/min. In figure 3a, MU03-blend with O<sub>2</sub> flow has endothermic curve at 180-210 °C that range was suitable melting point for conventional FDM 3D printer. Then, the MU03-blend was decomposed at 300-400 °C which weight suddenly decreased to zero and heat flow started endothermic curve again. It might be suggested that the blend was totally disappeared by heat. In figure 3b of CuFe-blend with O<sub>2</sub> flow, because the MU03 blend content have less than CuFe content, endothermic curve of melting point not occur. At 300-400 °C, weight of the CuFe-blend was almost reduced for 20% which totally polymer was disappeared by heat. Then, inter-particle metal was diffused with calcine to oxide in the same time. After 500 °C, the weight was increased up to 25% because oxidized metal was rapidly increased under O<sub>2</sub> flow condition, which metal oxide might be CuO and Fe<sub>3</sub>O<sub>4</sub> like equation (1)-(5). That temperature might be CuFeO<sub>2</sub> formation[16]. Then, CuFe<sub>2</sub>O<sub>4</sub> would be occurred at interface as long time as duration time like equation (6). The TGA result is similar to other copper base oxide [17-19] as the weight was increased up to 4%. Then, the sample continuously calcined in inert gas flow (N<sub>2</sub>) as shown in figure 3c. In addition, some the O<sub>2</sub> should be reacting with sample which Cu<sup>+</sup> was oxidized into Cu<sup>2+</sup> [18, 19]. CuFeO<sub>2</sub> could be appeared at interface between CuFe<sub>2</sub>O<sub>4</sub> and CuO like equation (7) because duration time of inert gas make CuFe<sub>2</sub>O<sub>4</sub> more stable state to CuFeO<sub>2</sub> [13] and weight was decreased because of removed defect in sample.

## 4. Conclusion

In summary, CuFeO<sub>2</sub> has been prepared by conventional 3D printing and sintering technique. Cu and Fe powder were mixed with a suitable polymer blend (MU03) which has 60.37 %v of metal content and extruded into 1.75 mm a FDM printing filament. Sample was calcined and sintered 700 °C under 1 atm O<sub>2</sub> and Ar gas flow respectively to get CuFeO<sub>2</sub>. XRD and DSC/TGA confirmed transformation and weight change of CuFeO<sub>2</sub>. This technique is a more convenient step for a complex shape ceramics fabrication. Their cost is cheaper and more potential for research and industries. In this report, CuFeO<sub>2</sub> phase and other oxide of metal compound phases were found in the 3D printing structure.

## 5. References

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