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# Synthesis and Characterization of Cu-Cr-O Phase with $H_2SO_4$ Solvent Using Sol-Gel Method

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**ABSTRACT**

Cu-Cr-O is a material with a delafossite structure and potentially good thermoelectric properties. This study synthesized Cu-Cr-O using the sol-gel method with $H_2SO_4$ acid solvent and Cu: Cr mole ratio of 2:1 through a 1000°C sintering process for 3 hours. Precursors used in this study were Copper (II) nitrate trihydrate ($Cu(NO_3)_2.3H_2O$), Chromium (III) oxide (Cr2O3), and urea ($C.O.(NH_2)_2$) according to the stoichiometric calculation. The precursor mixing process began by mixing ($Cu(NO_3)2.3H_2O$) and ($C.O. (NH_2)_2$). The precursor material ($Cr_2O_3$) was then solved using sulfuric acid following the stoichiometric calculation. The next step was the gel-making process, followed by the calcination and sintering stages. After that, the sample was crushed and compacted. XRD characterization was made to analyze the phase formation, and SEM characterization was made to analyze the microstructure of each sample. XRD characterization showed that using sulphuric acid and Urea ($C.O. (NH_2)_2$) addition resulted in the formation of the $CuCr_2O_4$ phase. The use of sulphuric acid formed $CuCr_2O_4$ with $Cr_2O_3$ and CuO as the contaminants.

**Keyword:** Calcination, Delafossite, Self-Combustion, Sintering, Sol-Gel

**ABSTRAK**

Cu-Cr-O adalah bahan dengan struktur delafossite dan sifat termoelektrik yang berpotensi baik. Pada penelitian ini, Cu-Cr-O disintesis menggunakan metode sol-gel dengan pelarut asam H2SO4 dan rasio mol Cu:Cr 2:1, melalui proses sintering 1000°C selama 3 jam. Prekursor yang digunakan dalam penelitian ini adalah Tembaga (II) nitrat trihidrat ($Cu(NO_3)_2.3H_2O$), Kromium (III) oksida ($Cr_2O_3$), dan urea ($CO(NH_2)_2$) sesuai perhitungan stoikiometri. Proses pencampuran prekursor dimulai dengan pencampuran ($Cu(NO_3)_2.3H_2O$) dan ($CO(NH_2)_2$). Bahan prekursor ($Cr_2O_3$) kemudian diselesaikan dengan menggunakan asam sulfat mengikuti perhitungan stoikiometri. Tahap selanjutnya adalah proses pembuatan gel yang dilanjutkan dengan tahap kalsinasi dan sintering. Setelah itu sampel dihaluskan dan dipadatkan. Karakterisasi XRD dilakukan untuk menganalisis pembentukan fasa, dan karakterisasi SEM dilakukan untuk menganalisis struktur mikro masing-masing sampel. Hasil karakterisasi XRD menunjukkan bahwa penggunaan asam sulfat dan penambahan Urea ($CO(NH_2)_2$) menghasilkan fasa $CuCr_2O_4$. Penggunaan asam sulfat membentuk $CuCr_2O_4$ dengan kontaminan $Cr_2O_3$ dan CuO.

**Kata Kunci:** Delafossite, Kalsinasi, Pembakaran sendiri, sintering, sol-gel

## 1. Introduction

Copper-based delafossite compounds, such as $CuAlO_2$, $CuCrO_2$, $CuGaO_2$, $Cu_2Y_2O_5$, and $CuFeO_2$, have gained growing attention from scholars due to their wide-gap p-type conductivity and catalytic properties [1]. Their physical property could also be modified by bringing an acceptable change in a chemical environment [2]. In this era, the application development of new materials plays a pivotal role in technological advancement and industries [3]. Cu-based delafossites possess multifunctional properties, including electrical, magnetic, optical, and thermal transport properties [2]. Some delafossites are interesting yet understudied, such as $CuFeO_2$, $CuCrO_2$, and $CuLaO_2$ [3]. The last few years have witnessed the rapid growth of intelligent touch devices and the significant evolution of flexible electronic and optoelectronic devices [1].

$CuCrO_2$ delafossite structure consisted of two alternating layers: The closed layer from CrO and a slightly distorted octahedral clamping plane of solid Cu in a halter in the form of linear coordination for oxygen anion in adjacent CrO [4]. The triangular lattice of $CuCrO_2$ gains broad attention due to its photoelectrical property without magnet field or doping at $Cr^{3+}$, unlike $CuFeO_2$ [5]. Various methods synthesize $CuCrO_2$ delafossite, each leading to different morphological and optoelectronic properties. In this category, solid-state, sol-gel, and hydrothermal syntheses are mainly used [5].

The sol-gel method is a common chemical to produce a highly pure powdery, thin film layers, fiber, monolith, and bulk structure material [6]. The gel is made through a polycondensation reaction, which continues until the sample turns into a gel, causing the solvent to shrink and form a solid mass [7].

The next step is to put the gel into the furnace and calcinate, in which the material is heated under its substantial temperature. The calcination process eliminates unwanted substances like nitrate, $CO_2$, and vapor from $CuCrO_2$, in addition to forming the precursor compounds for $CuCrO_2$ [8]. Sintering is a process that aims to form bonds between particles/ powder after the solidification process. It is done by heating a sample under its melting point until a mass transfer occurs on the powder surface, thus forming inter-powder cohesion [9]. Factors affecting the sintering result include temperature, time, environment, heating, and cooling rate [10]. In this study, XRD characterization was used to identify materials based on the crystal phase by determining the lattice constant and obtaining the grain size [11], while SEM characterization was used to observe the material surface in a high resolution [12].

## 2. Materials and Methods

The first step in this study was conducting stoichiometric calculation using Cu: Cr mole ratio of 2:1. The first precursor, i.e., 1.595 gr of Cu nitrate or $Cu(NO_3)_2.3H_2O$ was mixed with 0.3964 gr of urea or C.O. $(NH_2)_2$ until homogeneous. The second precursor, i.e., 0.5 g of $Cr_2O_3$, was dissolved with 15 ml of sulphuric acid in a hot plate using a magnetic stirrer at 210 rpm until homogeneous. Both precursors were mixed on a hotplate using a magnetic stirrer at 210 rpm and 90°C for two hours. The sample was then heated using a furnace at T=200°C for 24 hours until it turned into gel. The self-combustion process was done at 350°C for three hours. Before the calcination stage, the powdery sample was crushed in an agate mortar for three hours. The calcination process was done using Muffle Furnace at 780°C for three hours. The next step was the compaction process. In this stage, the sample was crushed for three hours and pelletized using a 250 MPa-pressing tool and followed by the sintering process at 1000°C for 3 hours.

## 3. Results And Discussion

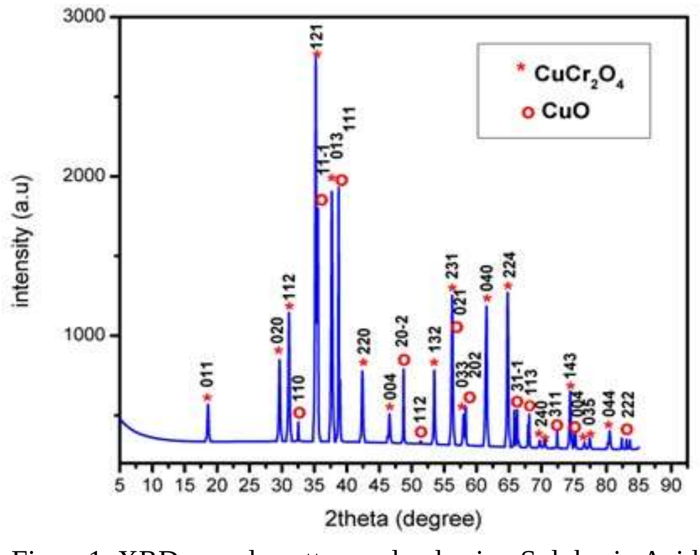


Figure1. XRD sample pattern solved using Sulphuric Acid

Figure 1 shows the diffraction peaks of Cu-Cr-O, followed by its miller indices. As shown in the figure, $CuCr_2O_4$ appeared as the dominant phase, and CuO appeared as the contaminant.

The XRD result showed that both samples have tetragonal crystal structures with the space group of I41/amd. Following the diffraction pattern, there were twenty-seven peaks in the first sample, with $CuCr_2O_4$ and CuO phases dominant. However, $CuCr_2O_4$ appeared more dominant, while CuO served as the contaminant. Table 1 presents the peaks of each phase and the crystallite size.

Table 1. Sample's crystallinity parameter.

| Sample | The formed phase (*XRD result*) | 2θ (deg) | Interplanar distance (*d*)(Å) | FWHM (*deg*) | Planar peak (*hkl*) | *Crystallite size* (*nm*) |
|---|---|---|---|---|---|---|
| Nitric | $CuCr_2O_4$ | 35.289 | 2.5413 | 0.231 | 121 | 36.08863 |
| acid | CuO | 38.841 | 2.3167 | 0.157 | 111 | 53.51689 |

Table 1 shows the difference in crystallite size of each sample. The largest crystallite size was noticed in the primary phase, with a value of 36.08863. The larger the FWHM value, the lower the crystallite size value, and the higher the FWHM, the more random the atom regularity [13].

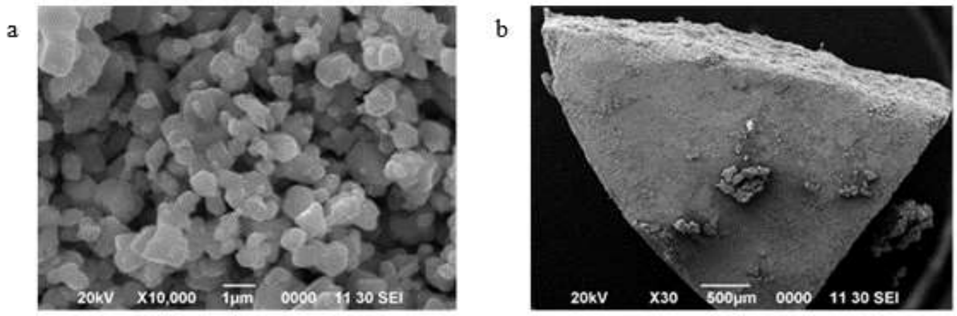


Figure 2. SEM Characterization Result

Figure 2 shows a stack of non-uniformed particles with irregular shapes, large particle sizes, and wide inter-particle cavities. It also shows that the crystal is in the form of small particles attached to the larger particles. This may occur because the pelletizing process was done on an uneven surface, in addition to other elements attached to the sample.

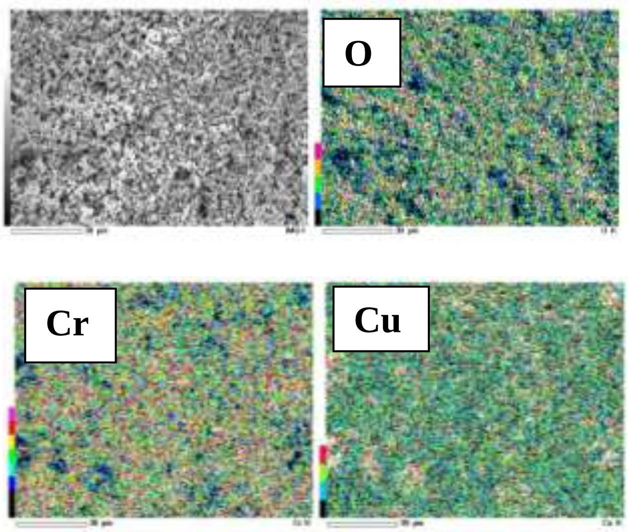


Figure 3. Sample mapping result

Figure 3 displays the distribution of each element on each sample. The right side of the Cu element exhibited a stack of white color, indicating a low concentration of Cu material. The Cr element at the left side exhibited a stack of black color, indicating that the Cr material is more dominant. Both samples exhibited different Cu and Cr element distributions.

The quantitative analysis result of the chemical composition distribution of the Cu-Cr-O sample with sulphuric and nitric acid as solvents could be seen from the EDX (Energy Dispersive X-ray) characterization.

Table 2. EDX result of Cu-Cr-O dissolved using Sulphuric acid

| Solvent | Element | % Atom |
|---|---|---|
| Sulphuric acid | Cu | 40.02 |
| | Cr | 44.35 |
| | O | 15.63 |

As shown in Table 2, the maximum atom domination was the Cr element, with a value of 44.35%. In other words, Figure 3 and Table 2 present a consistent result that Cr is the dominant element.

## 4. Conclusion

This study synthesized Cu-Cr-O materials with a sulphuric acid solution using the sol-gel method. The resulting phase was $CuCr_2O_4$, and no $CuCrO_2$ phase was noticed. The use of sulphuric acid formed $CuCr_2O_4$ with CuO as the contaminant.

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