



Synthesis and Characterization of Cu-Cr-O Phase with H₂SO₄ Solvent Using Sol-Gel Method

Syahrul Humaidi¹, Yusridah Rangkuti¹, Nurul Maulid¹, Agung Imaduddin², Satrio Herbirowo², Heri Nugraha², and Nono Darsono²

¹ Department of Physics, Faculty of Mathematics and Natural Science, Universitas Sumatera Utara, Medan, 20155, Indonesia

² Pusat Riset Material Maju, Badan Riset dan Inovasi Nasional Gedung 470I, Serpong, 15314, Indonesia

*Corresponding Author: syahrul@usu.ac.id

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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 H₂SO₄ 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(NO₃)₂·3H₂O), Chromium (III) oxide (Cr₂O₃), and urea (C.O.(NH₂)₂) according to the stoichiometric calculation. The precursor mixing process began by mixing (Cu(NO₃)₂·3H₂O) and (C.O. (NH₂)₂). The precursor material (Cr₂O₃) 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. (NH₂)₂) addition resulted in the formation of the CuCr₂O₄ phase. The use of sulphuric acid formed CuCr₂O₄ with Cr₂O₃ 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(NO₃)₂·3H₂O), Kromium (III) oksida (Cr₂O₃), dan urea (CO(NH₂)₂) sesuai perhitungan stoikiometri. Proses pencampuran prekursor dimulai dengan pencampuran (Cu(NO₃)₂·3H₂O) dan (CO(NH₂)₂). Bahan prekursor (Cr₂O₃) 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(NH₂)₂) menghasilkan fasa CuCr₂O₄. Penggunaan asam sulfat membentuk CuCr₂O₄ dengan kontaminan Cr₂O₃ dan CuO.

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

1. Introduction

Copper-based delafossite compounds, such as CuAlO₂, CuCrO₂, CuGaO₂, Cu₂Y₂O₅, and CuFeO₂, 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



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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 $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was mixed with 0.3964 gr of urea or C.O. $(\text{NH}_2)_2$ 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 $T=200^\circ\text{C}$ 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

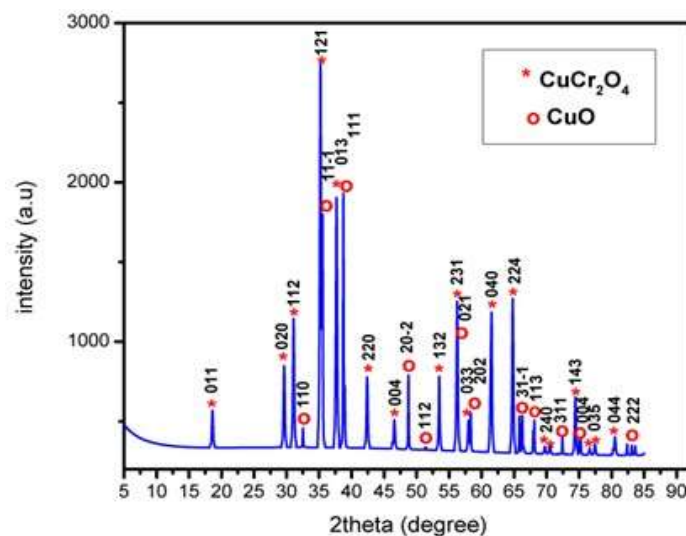


Figure1. XRD sample pattern solved using Sulphuric Acid

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 $I4_1/amd$. 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 acid	CuCr_2O_4	35.289	2.5413	0.231	121	36.08863
	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].

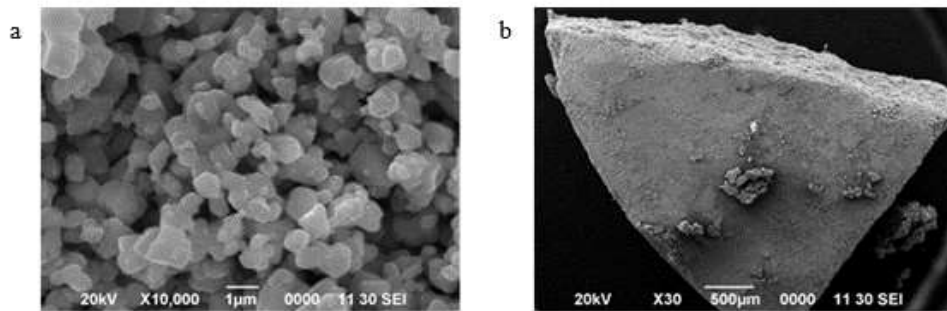


Figure 2. SEM Characterization Result

Figure 2 shows a stack of non-uniform 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.

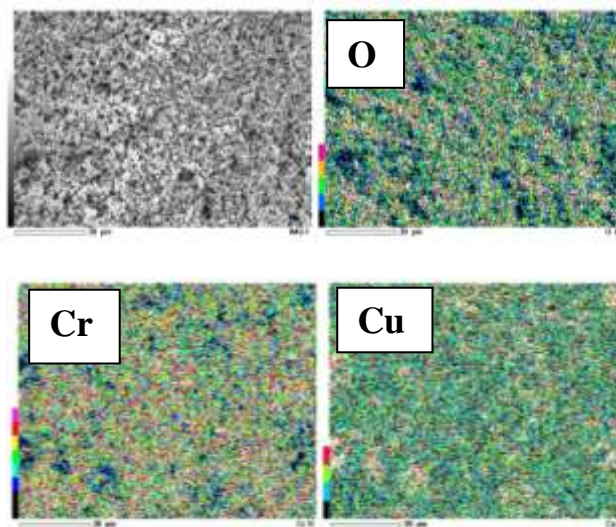


Figure 3. Sample mapping result

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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