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The Optimization of Copper Sulfate and Tincalconite Molar Ratios on the Hydrothermal Synthesis of Copper Borates

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***Abstract*—**In this research, copper borates are synthesized by the reaction of copper sulfate pentahydrate ($CuSO_4.5H_2O$) and tincalconite ($Na_2O_4B_7.10H_2O$). The experimental parameters are selected as 80°C reaction temperature and 60 of reaction time. The effect of mole ratio of $CuSO_4.5H_2O$ to $Na_2O_4B_7.5H_2O$ is studied. For the identification analyses X-Ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FT-IR) techniques are used. At the end of the experiments, synthesized copper borate is matched with the powder diffraction file of "00-001-0472" [$Cu(BO_2)_2$] and characteristic vibrations between B and O atoms are seen. The proper crystals are obtained at the mole ratio of 3:1. This study showed that simplified synthesis process is suitable for the production of copper borate minerals.

***Keywords*—**Hydrothermal synthesis, copper borates, copper sulfate, tincalconite.

I. Introduction

BORON is the chemical element with atomic number 5 and the chemical symbol B. The atomic mass is 10.81. It is a low-abundance element in both the solar system and the Earth's crust. Borate is the common name of the boron-containing minerals. General boron reserves of world can be classified as sodium borate, calcium borate, sodium-calcium borates and magnesium borates. Copper borates can be thought as special boron compounds due its low percentage of reserves in world. Natural copper borates reserves of world are the forms of Jacquesdietrichite ($Cu_2(H_2BO_3)(OH)_3$) in Morocco, Santarosaite (CuB_2O_4) and Bandylite ($Cu(B(OH)_4)Cl$) in Chile [1]-[4].

There are more than 150 types of boron minerals in nature. Tincalconite ($Na_2B_4O_7.5H_2O$) is the kind of boron mineral that has the B_2O_3 content of 47.8%. It can be used as both boron sources of industry and raw material of synthesis process for the specific boron compounds [1].

Copper sulfate is a kind of salt that exists as a series of compounds that differ in their degree of hydration. The anhydrous form is a pale green or gray-white powder, whereas the pentahydrate ($CuSO_4·5H_2O$), the most commonly encountered salt, is bright blue [5].

Copper borates are the member of both delafossite ($CuMO_2$) family and the metal borate groups [1], [6], [7]. With the lattice structure of copper borates that can be explained with a two-dimensional spin system; they exhibit specific features of optical transparency, high electrical conductivity (1.65 S/cm^2) and an indirect gap of 2.2 eV [8]. Copper metaborate $CuBO_2$ is considered a potential system. This is because of recent theoretical investigations, which predicts that the band gaps of $CuMO_2$ should increase as the ionic radius of *M* decreases. According to these predictions, $CuBO_2$ should have the largest band gap and hence better transmission characteristics. So they have the potential applications in the areas of superconductivity, transparent conductive oxides (TCOs) and diluted magnetic semiconductors [6], [7]. Also there are experiments about usage copper borates in preservation of wood materials, in catalysts of the dehydrogenation of organic compounds [9], [10].

Copper borate mineral can be synthesized at different structures of unit cells with the changing of experiment conditions. One of the typical copper borates [11] is $CuBO_2$, which can be seen in Fig 1. The synthesis procedures of copper borates generally involve thermal operations. The copper borate ($Cu_3B_2O_6$) was prepared by a solid-state reaction of copper oxide (CuO) and boric acid (H_3BO_3) at the reaction temperature of 900°C and time of 24 hours [12]. A kind of copper aluminum borate ($Cu_2Al_6B_4O_{17}$) was obtained via thermal synthesis method using copper sulfate ($CuSO_4$), aluminum sulfate octadecahydrate ($Al_2(SO_4)_3·18H_2O$), potassium sulfate (K_2SO_4) and H_3BO_3 [10]. Malavi et al., synthesized copper metaborate of CuB_2O_4 using the starting materials of $Cu(NO_3)_2.3H_2O$ and B_2O_3 at the reaction temperature of 500°C [13].

There also few studies about the preparation of copper borates via sol-gel method. Zheng et al, managed to synthesize the two different types of copper borates in nano-scale using sol-gel reactions of $CuSO_4.5H_2O$ and $Na_2O_4B_7.10H_2O$ between reaction temperatures of 10-70°C, although there are unknown impurities in structure [14]. In another sol-gel study, Santra et al., synthesized obtained the copper borates with reaction of CuO and B_2O_3 in the medium of citric acid at 75°C and 10 h [15].

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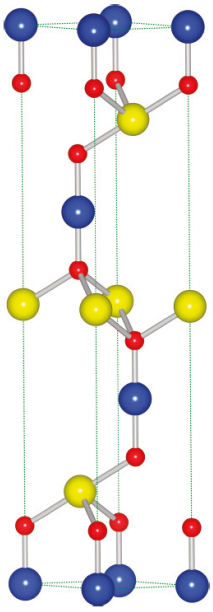

Fig. 1 Unit cell figure of rhombohedral $CuBO_2$. The red, blue, and yellow balls are oxygen, copper, and boron respectively [11]

In this study, copper borate mineral has been synthesized without using gelation agent in hydrothermal conditions. Applied synthesis process in literature has been simplified. The effect of molar ratio of starting materials ($CuSO_4.5H_2O$ to $Na_2O_4B_7.5H_2O$) to structure of obtained mineral has been investigated by identification and characterization methods of XRD and FT-IR.

II. Experimental

A. Materials and Method

Raw materials used in synthesis experiments were copper (II) sulfate pentahydrate ($CuSO_4.5H_2O$) and tincalconite ($Na_2O_4B_7.5H_2O$). $CuSO_4.5H_2O$ and $Na_2O_4B_7.5H_2O$ were provided from Merck Chemicals and Kırka Boron Management Plant (ETIMINE Kırka Works) in Eskisehir-Turkey, respectively.

Preparation method of copper borate used in study was hydrothermal synthesis method. The liquid phase of hydrothermal conditions was used as ultra-pure water (18.3 mΩ.cm) that was produced from the equipment of Human Power I^+ Water Purification System. Reaction temperature and time were selected as 80°C, and 1 hour, respectively; to investigate the interaction between raw materials according to the mole ratio changes. Determined molar ratios of $CuSO_4.5H_2O$ to $Na_2O_4B_7.5H_2O$ were 1:1, 2:1, 3:1, 4:1 and 5:1.

After the reaction, the filtration process was used for the removal of excess copper sulfate. In this process, distilled water was used for the washing and dispersing the synthesized copper borates below the filter paper. After that the slurry content was dried in Ecocell model oven at 60°C. The dried content was triturated for the characterization operations.

B. Characterization

Raw materials were subjected to X-Ray Diffraction (XRD) analysis with Philips PANanalytical brand (Fig. 2 (a)) where in this equipment X-rays are produced from Cu-Kα tube at the parameters of 45kV and 40mA [16].

Perkin Elmer Spectrum One (Fig. 2 (b)) Fourier Transform Infrared Spectroscopy (FT-IR) technique was used to determine which functional groups are presented in the samples. In the FT-IR technique Universal ATR sampling accessory – Diamond / ZnSe is used and measurement range is selected as 4000–650 cm^{-1}, scan number is 4 and resolution set as 4 cm^{-1} [16].

Fig. 2 (a) Philips PANanalytical XRD, (b) Perkin Elmer Spectrum One FT-IR

III. Results and Discussion

A. Raw Material Characterization Results

XRD patterns of the starting materials used in experiments are shown in Figs. 3 and 4 respectively. In the XRD pattern of copper sulfate pentahydrate (Fig. 3), the first three major peaks are seen in the 2θ values of 18.746°, 16.146° and 48.476°, respectively. In the XRD pattern of tincalconite (Fig. 4), the first three major peaks are seen in the 2θ values of 30.639°, 20.365° and 20.289°, respectively.

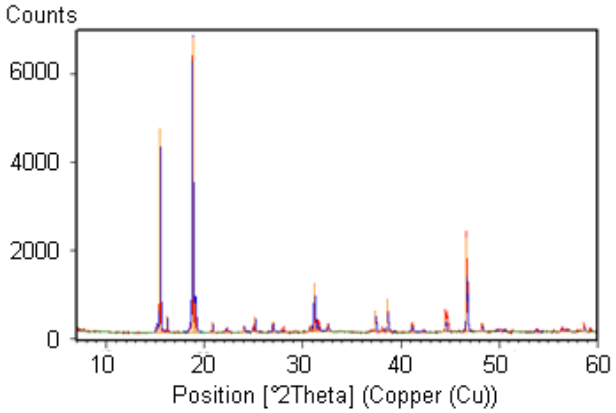

Fig. 3 XRD pattern of copper sulfate pentahydrate

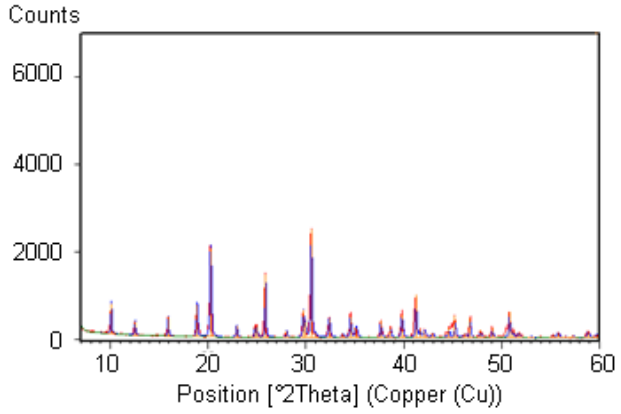

Fig. 4 XRD pattern of tincalconite

Results of XRD analyses are given in Table I. From the XRD results obtained it is seen that the raw materials used in experiments are identified as "01-077-1900" and "01-079-1529" pdf numbered "copper sulfate pentahydrate" and "tincalconite" minerals, respectively.

TABLE I
XRD RESULTS OF THE RAW MATERIALS

Mineral Name	Chemical Formula	Pdf #	Score
Copper Sulfate Pentahydrate	$CuSO_4.5H_2O$	01-077-1900	42
Tincalconite	$Na_2O_4B_7.10H_2O$	01-079-1529	74

FT-IR spectra of the $CuSO_4.5H_2O$ and $Na_2O_4B_7.10H_2O$ are shown in Fig. 5.

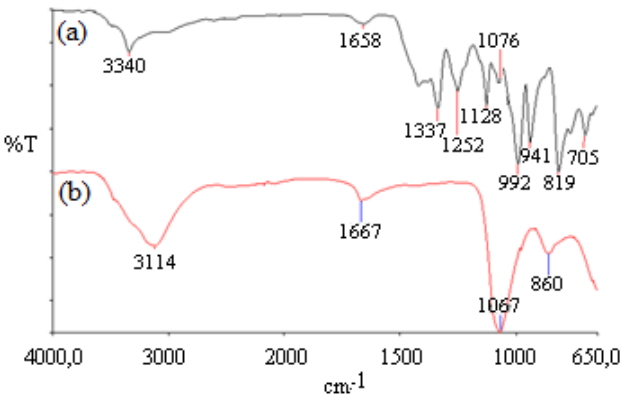

Fig. 5 FT-IR spectra of raw materials; (a) tincalconite, (b) copper sulfate pentahydrate

According to the FT-IR analysis of the tincalconite, characteristic peak are seen in the band values of 705, 819, 941, 992, 1076, 1128, 1252, 1337 and 1658 cm^{-1}. In the $CuSO_4.5H_2O$ spectrum have the characteristic peaks at the band values of 3114, 1667, 1063 and 860 cm^{-1}. In these spectra, the peaks over 3000 cm^{-1} may explain with the crystal water in structure. The peaks at lower band values can be explain with the vibrations between O and nonmetal atoms.

B. Synthesized Copper Borate XRD Results

XRD results and patterns of the synthesized copper borates are shown in Table II and, Fig. 6 respectively.

TABLE II
XRD RESULTS OF THE SYNTHESIZED COPPER BORATES

Mole Ratio	Pdf #	Mineral Name	Mineral Formula	Score
1:1	00-001-0472	Copper Borate	$Cu(BO_2)_2$	41
2:1	00-001-0472	Copper Borate	$Cu(BO_2)_2$	65
3:1	00-001-0472	Copper Borate	$Cu(BO_2)_2$	70
4:1	00-001-0472	Copper Borate	$Cu(BO_2)_2$	64
5:1	00-001-0472	Copper Borate	$Cu(BO_2)_2$	68

From the XRD results (Table II) obtained it is seen that "00-001-0472" pdf numbered "Copper Borate" mineral with the chemical formula of $Cu(BO_2)_2$ is formed at all experiments varying crystal scores. The highest XRD score is seen at the mole ratio of "3:1".

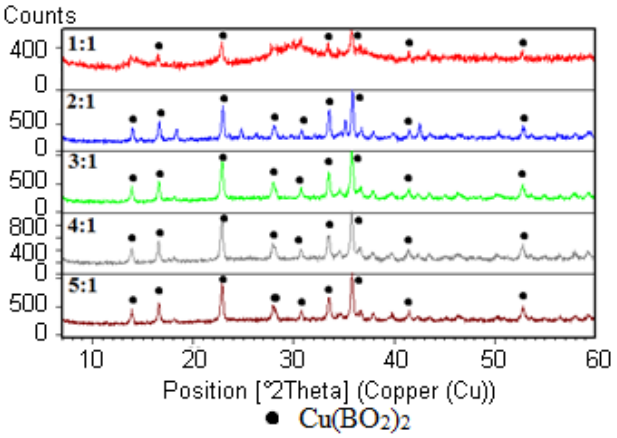

Fig. 6 XRD patterns of the synthesized copper borates

In Fig. 6, the first three major peaks of synthesized copper borate are seen in the 2θ values of 16.714°, 22.902° and 35.744°. Obtained peaks are not proper enough at the mole ratio of 1:1. With the increasing amount of copper sulfate in solution, proper peaks, which have similar band values of Copper Borate (00-001-0472 – $Cu(BO_2)_2$), are obtained. In the experiments for 4:1 and 5:1, minor changes in the structure of synthesized mineral are seen which may be due to excess copper sulfate pentahydrate in solution.

C. Synthesized Copper Borate FT-IR Results

FT-IR spectrums of synthesized minerals are shown in Fig 7. When vibrations in each spectrum are compared, it is seen that percentage changes in transmissions of synthesized copper borate minerals are similar except the spectrum of 1:1 (Fig. 7 (a)). This difference can be explained by the formation of insoluble byproducts in hydrothermal media. Thus, it may not be separated by filtration stage. These peaks are seen between band values of 1404 and 1231 cm^{-1} in the FT-IR spectra for mole ratio 1:1.

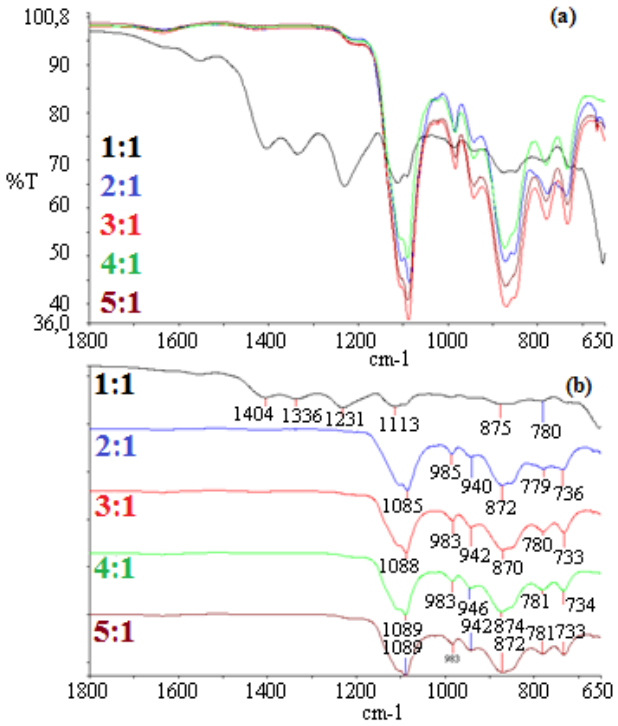

Fig. 7 FT-IR spectrum of synthesized minerals (a) overlaid, (b) split

In Fig. 7 (b), the peaks between 1120–980 cm^{-1} might be the asymmetric stretching of tri-coordinate boron ($B_{(4)}$–O). Symmetric stretching of $B_{(3)}$–O can be seen between 980–870 cm^{-1}. Symmetric stretching of tri-coordinate boron ($B_{(4)}$–O) can be seen in the band values of approximately 780 cm^{-1}. Other peaks which have values lower than 750 cm^{-1} explains the bending of $B_{(3)}$–O in the structure.

Obtained vibration band values are compatible with the previous studies in literature [17].

IV. Conclusions

Boron found in nature in the combinations of other elements. Majority of boron reserves are found in Turkey (%73). Copper borates are a sub-group of boron minerals and have the usage fields of superconductivity, transparent conductive oxides (TCOs) and diluted magnetic semiconductors due to their optical and magnetic properties.

In literature copper borate synthesis have complex processes. The novelty of this research is the synthesis of copper borate using simplified processes. The effect of mole ratio to synthesis of copper borates is investigated and optimum mole ratio is determined in light of characterization analyses. These experiments can be seen as a preliminary step.

In future studies, copper borate synthesis at higher crystallinity and different structures are intended with the optimization of reaction temperature and time.

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