JOTCS A
Journal of the Turkish Chemical Society
Section: A
Chemistry
TURKISH CHEMICAL SOCIETY

Sonochemical Synthesis of Copper Borates: Effect of Reaction Conditions on the Characteristic Properties

Fatma Tuğçe Şenberber Dumanli[1], Sibel Kavci Karaagac[2], Azmi Seyhun Kipcak[2], Emek Moroydor Derun[2*]

[1]Istanbul Nisantasi University, Department of Civil Engineering, Istanbul, 34398, Turkey
[2]Yildiz Technical University, Department of Chemical Engineering, Istanbul, 34210, Turkey

Abstract: The effect of ultrasonic treatment on liquid-state production and the characteristic features of synthesized powder were studied in liquid-state conditions. In sonochemical synthesis, the operation parameters of mole ratio, reaction temperature, and time were optimized. The synthesis was achieved in moderate conditions such as mole ratio of copper: sodium: boron (Cu: Na: B) 1:2:1, 70°C and 2.5 minutes. The prepared samples were identified as copper borate ($Cu(BO_2)_2$) with the powder diffraction file number "00-001-0472". The reaction yields were also increased from 50% to 71.5% with the modification of the experimental procedure. The specific FT-IR peaks were observed at 1090, 985, 872, 781 and 731 cm-1 band values. In the morphological analyses, the agglomerations of multi-angular particles were seen. The results showed the affirmative effects of the possible use of the ultrasonic treatment on both the practical synthesis and the increase of characteristics.

Keywords: Copper; Borate; X-ray methods; Spectroscopy; SEM; Ultrasound.

Submitted: August 9, 2023. **Accepted**: November 20, 2023.

Cite this: Şenberber Dumanli FT, Kavci Karaagac S, Kipcak AS, Moroydor Derun E. Sonochemical Synthesis of Copper borates: Effect of Reaction Conditions on the Characteristic Properties. JOTCSA. 2024;11(2):461-6.

DOI: https://doi.org/10.18596/jotcsa.1342058

***Corresponding author.** E-mail: moroydor@yildiz.edu.tr

1. INTRODUCTION

Metal borates are defined as compounds including metal atoms, boron, oxygen, and hydrogen, if any. Commonly, three coordinated trigonal and four coordinated tetragonal groups of boron and oxygen are bonded to metal atoms. The metal borates can be defined according to the metal atom in structure (1). As a member of the borate family, copper borates occur from the different combinations of copper and boron atoms such as $CuBO_2$, $Cu(BO_2)_2$, $Cu_3B_2O_6$, and $3CuO{\cdot}2B_2O_3{\cdot}6H_2O$ (2). The fabrication of copper borates draws attention because of their unique crystallographic structures, and they exhibit electrical, magnetic, and optical features (3). Among the delafossite group compounds, copper borates have the largest band gap (4,5). Copper borates are mostly utilized in linear and non-linear optical devices, hydrogen generation systems, and photocatalytic reactions. Also, this type of borate has applications in fire retardants, wood preservation, the design of ion exchange materials, and lubricant additives (6–9). These characteristics make their synthesis important. Different procedures were experimented with to synthesize the copper borate at different compositions and characteristics, such as supercritical, hydrothermal, solvothermal, and solid-state (10–12). With the optimization of reaction conditions, the modified particle fabrication of copper borates could be probable (13,14).

Alp et al. indicated the effects of pH on the colorimetric features of synthesized powder, and the darker samples were prepared in alkaline conditions (2). Pisarev et al. characterized the piezoelectric form of copper borate in tetragonal lattice (6). Kahalili et al. studied the catalytic activities of boron-containing copper complexes in organic reactions (15). Kipcak et al. studied the effect of copper and boron sources on the prepared sample using a traditional hydrothermal method (16).

The studies on copper borate clarified the importance of optimizing the parameters to obtain the sample at the highest reaction yield and crystallinity. As a developing technology, ultrasound treatment can be used to increase contact of raw material in liquid-state conditions. With the use of ultrasound treatment in the synthesis procedure, the required reaction time and temperature can be decreased, whereas the reaction yield and crystallinity of the sample can be increased (17). In this paper, it is aimed to investigate the suitability of sonochemical synthesis for copper borate fabrication without using any modification agent. Also, the effect of reaction conditions on the characteristics of prepared copper borate was studied by using the techniques of X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FT-IR), and Scanning Electron Microscope (SEM).

2. EXPERIMENTAL SECTION

2.1. Materials

The copper source used in the experiments was copper sulphate pentahydrate ($CuSO_4{\cdot}5H_2O$) purchased from Sigma Aldrich at a minimum purity of %98. Boron source of boric acid (H_3BO_3), with a minimum purity of %99, was provided by Eti Mine Boron Works in the region of Bandirma, Turkey. Sodium hydroxide (NaOH) was obtained from Merck Chemicals at the minimum purity of %97.

2.2. Synthesis

In liquid-state conditions, the probable reaction can be seen in Eq. 1, and the experimental design is presented in Figure 1. The experimental procedure could be explained in two steps. In the first step, the starting materials were dissolved in distilled water and reacted with the effect of ultrasound at 80°C for 5 minutes. For the sonochemical synthesis, an ultrasonic probe of Bandelin was employed. The determined molar ratios of $CuSO_4{\cdot}5H_2O$: NaOH: H_3BO_3 were 1:2:0.8, 1:2:1, 1:2:1.33, 1:2:2, and 1:2:4. In the second step of the synthesis, the effect of temperature and time were examined. The samples were prepared at the reaction temperatures of 70, 80, and 90°C for the reaction times of 2.5, 5, 10, and 15 minutes. After the reaction was completed, the solutions were washed, filtered, and dried in an Ecocell incubator.

$$CuSO_4 \cdot 5H_2O(aq) + 2NaOH(aq) + 2H_3BO_3\ (aq) + xH_2O(l) \rightarrow CuB_2O_4(aq) + Na_2SO_4\ (aq) + (9+x)H_2O(l) \quad \text{(Eq. 1)}$$

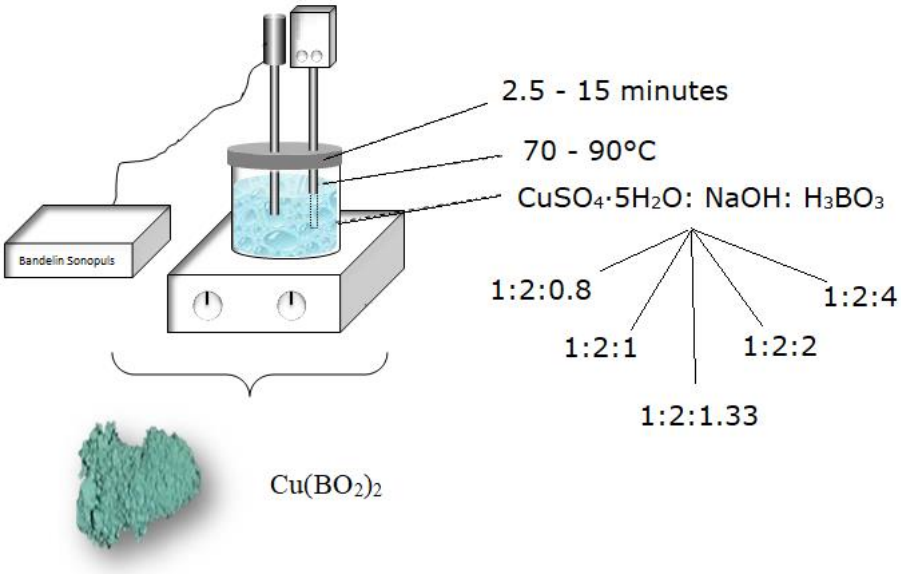


Figure 1: The experimental design for the sonochemical synthesis of copper borates

2.3. Characterization of the Synthesized Samples

The prepared powders underwent X-ray diffraction analysis for the identification of obtained phases by using a PANalytical Xpert Pro X-Ray Diffractometer at the operating conditions of 45 kV, 40 mA, and in the 2θ range of 10 - 70°. In the characterization of functional groups of structure, the samples were subjected to Fourier Transform Infrared (FT-IR) Spectroscopy by using a Jasco 6000 Fourier Transform Infrared Spectrometer. For the morphological characterization, the Scanning Electron Microscope of Tescan Vega 3 (SEM) was used at the operating conditions of 15 kV and magnification values of 400 X.

In estimating reaction yields, $CuSO_4{\cdot}5H_2O$ was identified as the key component in the experiments. Typically, the product moles at the last stage, N_P, were divided by the consumed moles of the key reactant, A, to calculate the overall yield, Y. The moles of A that were consumed were determined by using the reactant's final (NA) and initial (NA0) moles. For a batch system, the calculation of reaction yield was given in Eq. 2 (18).

$$Y = \frac{N_P}{N_{A0} - N_A} \quad \text{(Eq. 2)}$$

3. RESULTS AND DISCUSSION

3.1. XRD Results

In the XRD analyses, the obtained phases matched $Cu(BO_2)_2$ with the powder diffraction file number "00-001-0472". XRD patterns of the mole ratio experiments are shown in Figure 2. XRD patterns indicated the lower peaks formation of crystalline phase in the mole ratio (Cu: Na:B) of 1:2:0.8. At the 1:2:1 ratio, the characteristic peaks were observed at the 2θ values of 13.82°, 16.71°, 22.90°, 28.13°, 33.67°, 35.74° and 52.89°. Counts of the obtained peaks were in decline at the higher ratios of boric acid, and the sample was identified as amorphous at the ratio of 1:2:4.

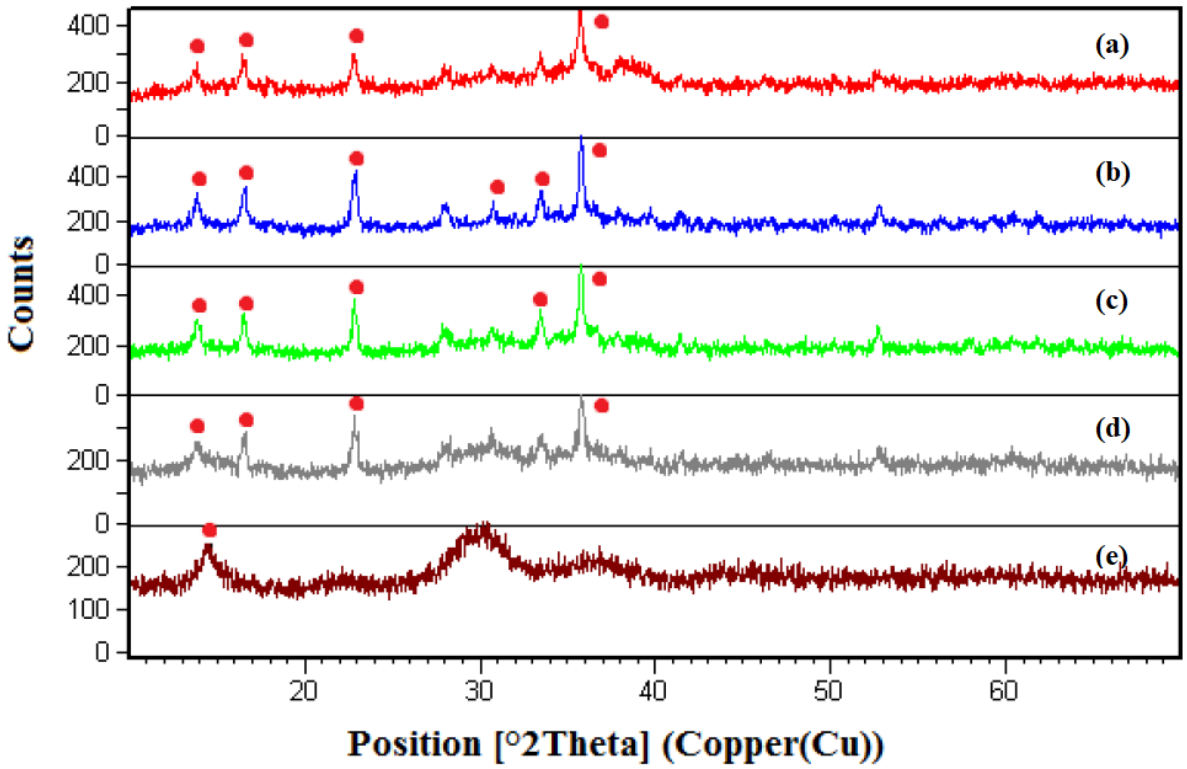


Figure 2: XRD patterns of the mole ratio experiments (a) 1:2:0.8, (b) 1:2:1, (c) 1:2:1.33, (d) 1:2:2, and (e) 1:2:4.

At the mole ratio of 1:2:1, the XRD scores of the samples at different temperatures and times are given in Table 1. According to the XRD results, the optimum reaction conditions were determined to be 70°C and 2.5 minutes. Compared with the traditional hydrothermal synthesis procedure, ultrasonic treatment in the experimental procedure positively affected the formation and decreased the reaction time (16).

Table 1: XRD scores of the samples at different temperatures and times.

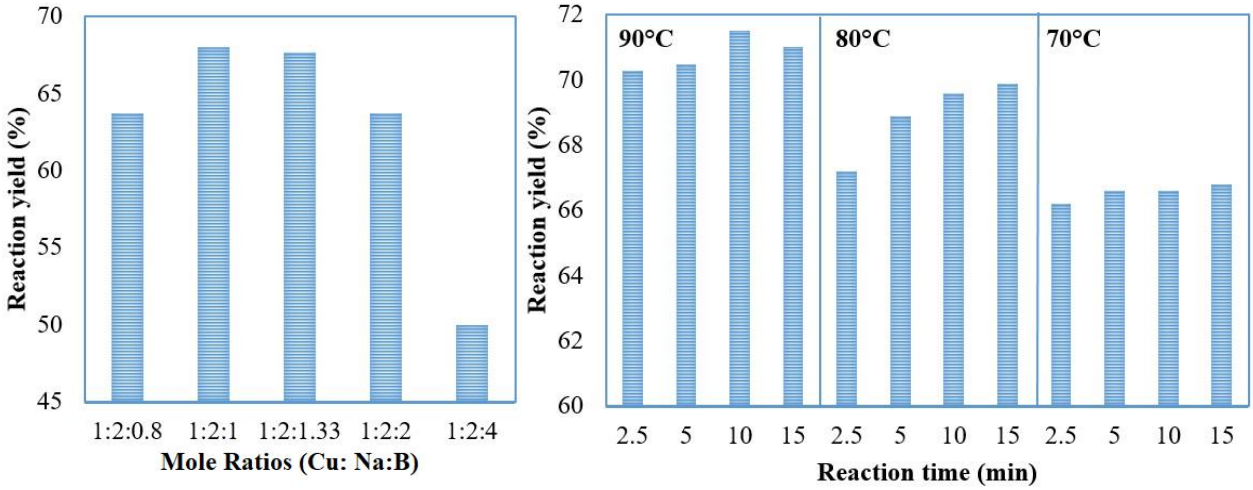
Temperature (°C)	Time (min)	XRD Score
90	2.5	38
	5.0	*
	10	25
	15	*
80	2.5	30
	5.0	13
	10	25
	15	40
70	2.5	41
	5.0	27
	10	*
	15	*

3.2. The Results of Reaction Yields

The plots of reaction yield percentages with the changing reaction parameters, such as mole ratios, reaction time, and temperature, can be seen in Figure 3. The effect of the mole ratio of the sources can be seen in the reaction yield as well as crystallinity (Figure 3 (a)). The calculated reaction yield percentages were in the range of 50 – 71.5%. Among the different mole ratios, the highest reaction yield percentage was obtained at the ratio of 1:2:1. In Figure 3 (b), minor increases were obtained with increasing temperature and time. The highest reaction yield was estimated to be 71.5% at the reaction temperature of 90°C and 15 mins.

3.3. FT-IR results

The characteristic band values observed in the IR range of the prepared sample at 70°C and 2.5 minutes were presented in Figure 4. According to the FT-IR results, the peaks between 1090 and 985 cm-1 are related to the asymmetrical stretching of four-coordinate boron to oxygen bands [$\upsilon_{as}(B_{(4)}$-O)]. The stretching observed at 872 cm^{-1} can be explained by the symmetrical stretching of three-coordinate boron to oxygen bands [$\upsilon_{s}(B_{(3)}$-O)]. The characteristic band values in the range of 781 and 731 cm^{-1} indicated the symmetrical stretching of four-coordinate boron to oxygen bands [$\upsilon_{s}(B_{(4)}$-O)].



(a) (b)

Figure 3: Reaction yields at (a) different mole ratios (1:2:0.8, 1:2:1, 1:2:1.33, 1:2:2, and 1:2:4) and (b) different reaction temperatures and times (70, 80, and 90°C; 2.5, 5, 10, and 15 minutes).

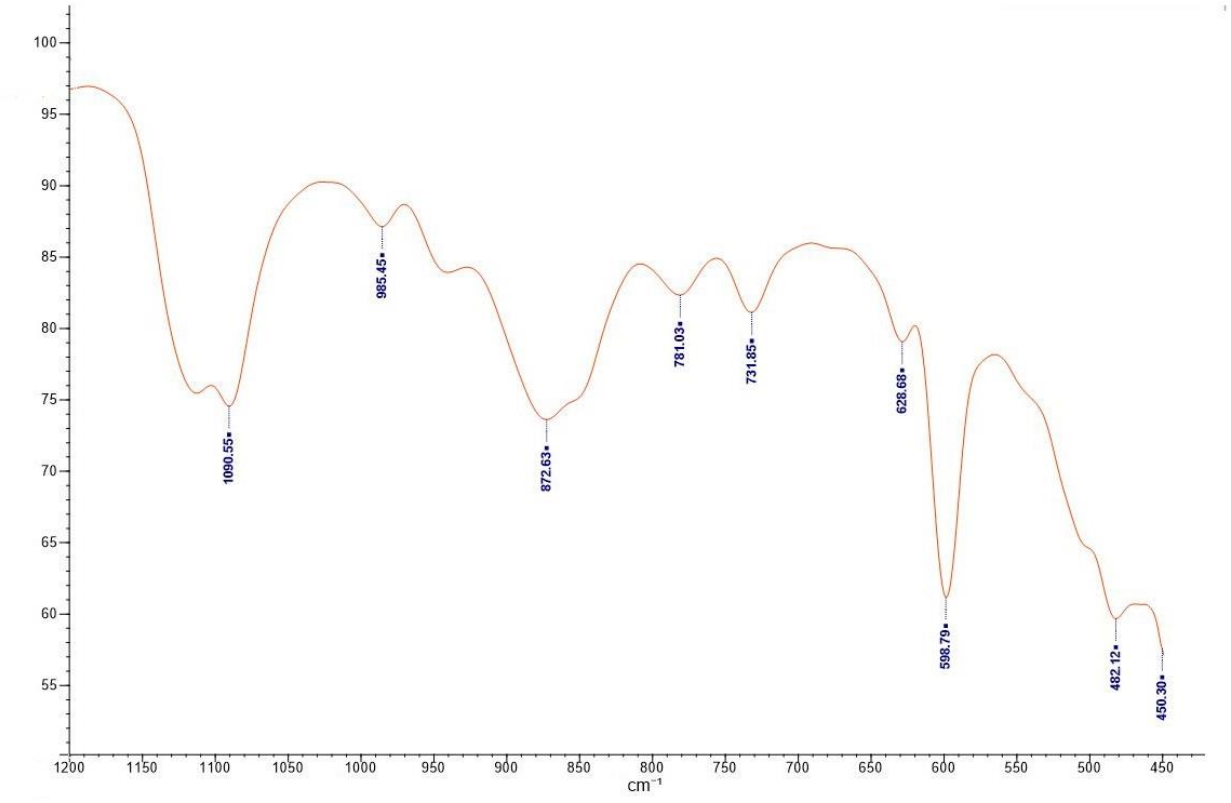


Figure 4: FT-IR spectrum of the prepared sample at 70°C and 2.5 minutes.

From the spectral results obtained, it is seen that the specific boron to oxygen bands were achieved in the preparation and that these B to O bands are in good agreement with Zheng et al. and Yongzhong et al. (14, 19).

3.4. SEM results

The morphology of the prepared sample at 70°C and 2.5 minutes was given in Figure 5. With the effect of intramolecular hydrogen bonding, the agglomeration of sub-micron scale particles could be seen in the SEM results. The multi-angular particle formation could explain the morphology of the sample.

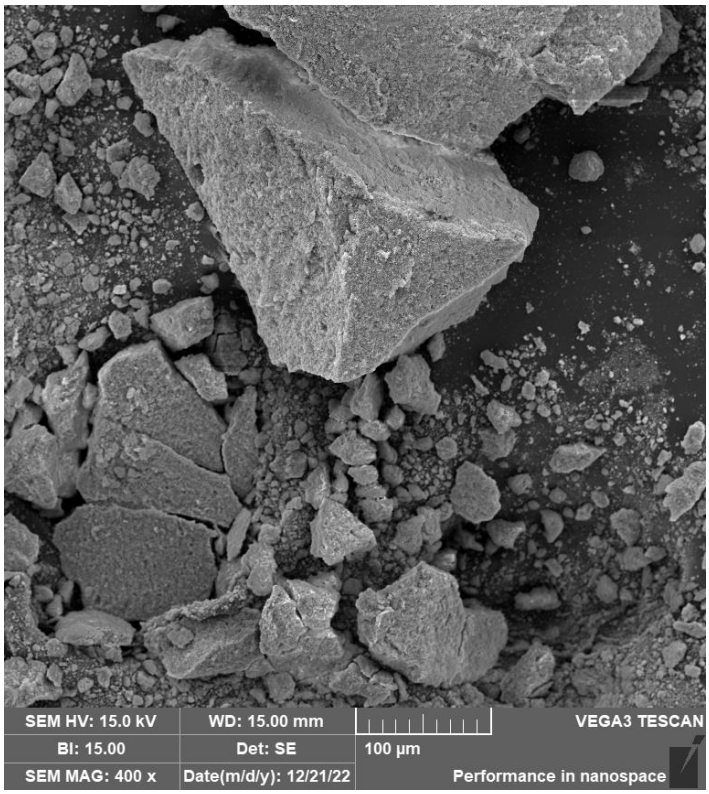


Figure 5: Morphology of the prepared sample at 70°C and 2.5 minutes.

The obtained morphology was in good agreement with the previous studies. Compared with the traditional liquid-state synthesis method, homogeneity in the surface was observed (16).

4. CONCLUSION

The copper borate ($CuBO_2)_2$) was successfully synthesized in moderate liquid-state conditions with the help of ultrasonic treatment. The reaction conditions were optimized for the modified experimental procedure, and the possible reaction mechanism was estimated. The optimum reaction parameters can be summarized as the mole ratio (Cu:Na:B) of 1:2:8, the reaction temperature of 70°C, and a reaction time of 2.5 minutes. The experimental results indicated the beneficial effects of ultrasonic treatment on the characteristic features of the prepared sample. The temperature also increased the reaction yield; however, the crystallinity decreased. This situation can be interpreted as being temperature-**sensitive** to the obtained phases. The reaction time was decreased, and the fabricated powder's crystallinity was increased with the help of ultrasonic treatment. The obtained characteristic band values of FT-IR were in good agreement with the previous studies.

5. CONFLICT OF INTEREST

The author declares no conflict of interest.

6. REFERENCES

1. Senberber FT, Derun EM. Thermal Kinetics and Thermodynamics of the Dehydration Reaction of Inyoite ($Ca_2B_6O_6(OH)_{10} \cdot 8H_2O$). Glass Phys Chem. 2020;46(1):64-71. Available from: <URL>

2. Alp B, Atakul Savrik S, Balkose D. Preparation and Characterization of Copper Borates as Lubricant Additives. J Mater Sci Eng B. 2014;4(4). Available from: <URL>

3. Thatribud A, Tungsurat T, Pengpan T. First-principles study on electronic and optical properties of transparent conducting oxide $CuBO_2$. Comput Mater Sci. 2014;81:601-6. Available from: <URL>

4. Zia W, Siraj K, Faiz H, Firdos A. A facile synthesis of single phase delafossite CuBO $_2$ powders. Mater Res Express. 2019; 6(9):096314. Available from: <URL>

5. Santra S, Das NS, Maiti S, Chattopadhyay KK. Wide band gap p-type $CuBO_2$ nanostructures by hydrothermal route and fabrication high quality p-$CuBO_2$/n-ZnO nano-heterojunction. Chem Phys Lett. 2014;604:97-100. Available from: <URL>

6. Pisarev RV, Boldyrev KN, Popova MN, Smirnov AN, Davydov VYu, Bezmaternykh LN, vd. Lattice dynamics of piezoelectric copper metaborate CuB_2O_4. Phys Rev B. 2013;88(2):024301. Available from: <URL>

7. Liu LL, Zhu D, Cao LL, Stephan DW. N-Heterocyclic carbene stabilized parent sulfenyl, selenenyl, and tellurenyl cations (XH^+, X = S, Se, Te). Dalton Trans. 2017;46(10):3095-9. Available from: <URL>

8. Soylu M, Al-Ghamdi AA, Omran SB, Yakuphanoglu F. Rectifying structure with high voltage operation based on $CuBO_2$ as an UV photocatalyst. J Alloys Compd. 2014;617:602-8. Available from: <URL>

9. Zhang HH, Kong N, Wang J, Liu ZH. Thermodynamic properties of microporous materials for two copper borates, MCuB7O12·H2O (M=Na,K). J Chem Thermodyn. 2015;89:164-8. Available from: <URL>

10. Hu ZS, Dong JX, Chen GX, Lou F. Preparation of nanometer copper borate with supercritical carbon dioxide drying. Powder Technol. 1999;102(2):171-6. Available from: <URL>

11. Szwagierczak D, Synkiewicz-Musialska B, Kulawik J, Pałka N. Sintering, Microstructure, and Dielectric Properties of Copper Borates for High Frequency LTCC Applications. Materials. 2021;14(14):4017. Available from:https://www.mdpi.com/1996-1944/14/14/4017

12. Wang JJ, Wei Q, Yang BF, Yang GY. Two New Copper Borates with Mesoscale Cubic Supramolecular Cages Assembled from $\{Cu_4@B_{20}\}$ Clusters. Chem - Eur J. 2017;23(12):2774-7. Available from: <URL>

13. Ursu D, Dabici A, Miclau M, Miclau N. Low-temperature hydrothermal synthesis of hierarchical flower-like CuB_2O_4 superstructures. Process Appl Ceram. 2020;14(2):113-8. Available from: <URL>

14. Zheng Y, Wang Z, Tian Y, Qu Y, Li S, An D, vd. Synthesis and performance of 1D and 2D copper borate nano/microstructures with different morphologies. Colloids Surf Physicochem Eng Asp. 2009;349(1-3):156-61. Available from: <URL>

15. Khalili D, Evazi R, Neshat A, Aboonajmi J. Copper(I) Complex of Dihydro Bis(2-Mercapto Benzimidazolyl) Borate as an Efficient Homogeneous Catalyst for the Synthesis of 2 *H* -Indazoles and 5-Substituted 1 *H* -Tetrazoles. Chemistry Select. 2021;6(4):746-53. Available from: <URL>

16. Kipcak AS, Senberber FT, Aydin Yuksel S, Derun EM, Piskin S. Synthesis, characterisation, electrical and optical properties of copper borate compounds. Mater Res Bull. 2015;70:442-8. Available from: <URL>

17. Senberber Dumanli FT, Moroydor Derun E. A comparative study of ultrasonic-assisted methods to synthesise spinel ($CoAl_2O_4$) nanoparticles. Ceram Int. 2022;48(13):19047-55. Available from: <URL>

18. Fogler HS. Elements Of Chemical Reaction Engineering. Prentice Hall India; 1999. 1004 s.

19. Yongzhong J, Shiyang G, Shuping X, Jun L. FT-IR spectroscopy of supersaturated aqueous solutions of magnesium borate. Spectrochim Acta A Mol Biomol Spectrosc. 2000;56(7):1291-7.