Special Issue of the 8th International Advances in Applied Physics and Materials Science Congress (APMAS 2018)

Obtainment of Copper(II) Fluoroborate by High-Energy Impacted Ball-Milling

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In this study, copper(II) fluoroborate, one of the special boron products, was synthesized by high energy impacted ball milling method and characterization studies were carried out by means of FTIR and BF_4^- ion selective electrode. Copper fluoride and elemental boron were used as reactants in the study. Mechanochemical method by means of ball milling was carried out, in a three-dimensional spex-type ball mill in an argon atmosphere. Specimens were prepared at different mole ratios and mechanically milled in a ball mill for a fixed time to determine the optimum mole ratio and the reaction period was optimized in the next step. As a result of the experiments, the most efficient reaction was obtained when reactant mole ratio (n_B/n_{CuF_2}) of 0.85:1 and reaction period of 1500 minutes. Copper(II) fluoroborate was produced with a yield of 84.5% under the optimum conditions.

DOI: 10.12693/APhysPolA.135.888

PACS/topics: copper(II) fluoroborate, ball milling, mechanochemical reaction, copper fluoride, boron

1. Introduction

As industrialization and technological developments increase; the search for functional material which is eco-friendly, non-toxic, high temperature and flame resistant is also increasing. Boron is one of the indispensable mineral resources which can respond the all of these needs, having strategic importance and one of the main input materials of the growing industrial and technological progress. Apart from raw and refined products, there are special boron compounds which are produced for commercial purposes by using generally refined boron products with high technology required methods. Fluoroborates are important special boron compounds. Fluoroborate salts are obtained by reaction of oxides, hydroxides, carbonates and fluorides with boric acid or fluoroboric acid [1]. As another production method, stable fluoroborates can be also formed by reacting boron fluoride with metal fluorides [2]. Fluoroborates are commercially significant for various industries. Main group metals, transition metals and other heavy metal fluoroborate salts and ammonium fluoroborates are used in different fields. Fluoroborates are used as catalyst in different reactions. Copper(II) fluoroborate is one of the most useful catalysts in organic reactions [3]. Fluoroborates are used in with using rare earth ions to improve the properties of glasses [4]. Fluoroborates are used as electrolyte [5]. Fluoroborates give flame retardant properties to materials and they are used as flame retardant in synthetic fibers, polymers [6] and textile materials etc. [7].

In this study, copper(II) fluoroborate was produced by ball milling. Mechanochemical synthesis by means of ball milling of materials is the general name given to the grinding of metal powders containing chemical reactions that occur during milling. High energy impacted ball mills are used for mechanochemical reactions. There is a set of important parameters which effect mechanochemical reaction. These are type of mill, milling atmosphere, ball-to-powder weight ratio, milling container, milling speed, type, size and milling period etc. [8].

The aim of this work was to investigate the obtainment of synthetic copper(II) fluoroborate by using high-energy impacted ball milling. It is a novel synthesis method for the production of the copper(II) fluoroborate under argon atmospheric conditions using copper fluoride and boron as reactants by mechanochemical reaction.

2. Experimental procedure

Copper(II) fluoroborate was synthesized by mechanochemical reaction of copper fluoride (98% pure, Sigma-Aldrich 217905) and boron ($\geq$ 95% pure, Merck 1120700025) in high energy impacted ball mill. High purity commercial copper(II) fluoroborate was bought from Sigma-Aldrich (366587).

Different size of balls were used with stainless reactors. Reactants were placed in steel reactors in a glove box (Plas. Labs. Simplicity 888) in an argon atmosphere. High-purity argon is the most common ambient to prevent oxidation and contamination of the powder. The ball to sample mass was fixed 4:1. The reaction was carried out at room temperature. The reaction that takes place in copper(II) fluoroborate production by mechanochemical method is as given in the following Eq. (1):

$$4CuF_2 + 2B \rightarrow Cu(BF_4)_2 + 3Cu \quad (1)$$

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During the experiments the effect of reactant mole ratio and reaction period on product yield were investigated. The optimum conditions were determined by investigating reactant mole ratio and reaction period as parameters. In order to determine the optimum mole ratio of B/CuF_2, the samples were prepared different mole ratios which were in the range of 0.45–1.0 according to stoichiometric coefficient and reaction period was fixed during the experiments. Optimum reactant mole ratio was kept constant and the optimum reaction period was determined by continuing experiments at different reaction periods. The reaction periods were changed from 1000 to 2000 min. Characterization studies were conducted by Fourier transform infrared spectroscopy (Jasco FTIR-480+) and BF_4^- ion selective electrode (DX287-Mettler Toledo). Synthetic copper(II) fluoroborate sample was tried to analyze by XRD instrument (Rigaku).

3. Results and discussion

Different amounts of commercial copper(II) fluoroborate were pressed with KBr (Merck 104907) for FTIR analysis. FTIR spectrum of commercial copper(II) fluoroborate was given at Fig. 1a. Characteristic FTIR absorption band of B–F is 1000–1100 cm^{-1} range [9]. The scanned area shown in Fig. 1a is the peak of the B–F bond. Calibration graph was generated by using the amount of copper(II) fluoroborate and the B–F bond FTIR peak area. The calibration graph of commercial copper(II) fluoroborate is given in Fig. 1b. Calibration curve was used to determine the product yield.

FTIR spectroscopy is a technique used for solid-state analysis [10]. FTIR instrument is used for both qualitative and quantitative analysis [11, 12]. In this study, both of them were investigated. FTIR analyzes of samples prepared at different reactant mole ratios were performed. The FTIR spectrums of the samples are shown in Fig. 2. As can be seen from Fig. 2, the highest intensity was observed the sample which had 0.85 reactant mole ratio (n_B/n_{CuF_2}).

FTIR peak areas were used to calculate the yields. The yields for whole mole ratio (B/CuF_2: 0.45–1.0 at 1000 minutes reaction period) were given in Fig. 3a. The optimum yield was obtained when the ratio was kept as 0.85. It was observed that the yield increased up to optimum mole ratio value. The yield is 65.2% when reactant mole ratio is 0.85. But after this value, the decrease in yield was observed as the mole ratio increased. It is thought that the reason for the drop in yield is due to the dilution of the medium because of the excess reactant.

BF_4^- ion-selective electrode is sensitive to tetrafluoroborate ion. Low levels of BF_4^- ion can be determined by using BF_4^- ion selective electrode [13]. The fluoroborate ion concentration was determined utilizing copper(II) fluoroborate solubility in water. The BF_4^- ion selective electrode was used to determine the BF_4^- ion concentration. Solutions were prepared at different mole ratios and analyzed with ion selective electrode. The BF_4^- ion concentrations and the yields were found as shown in Fig. 3b.

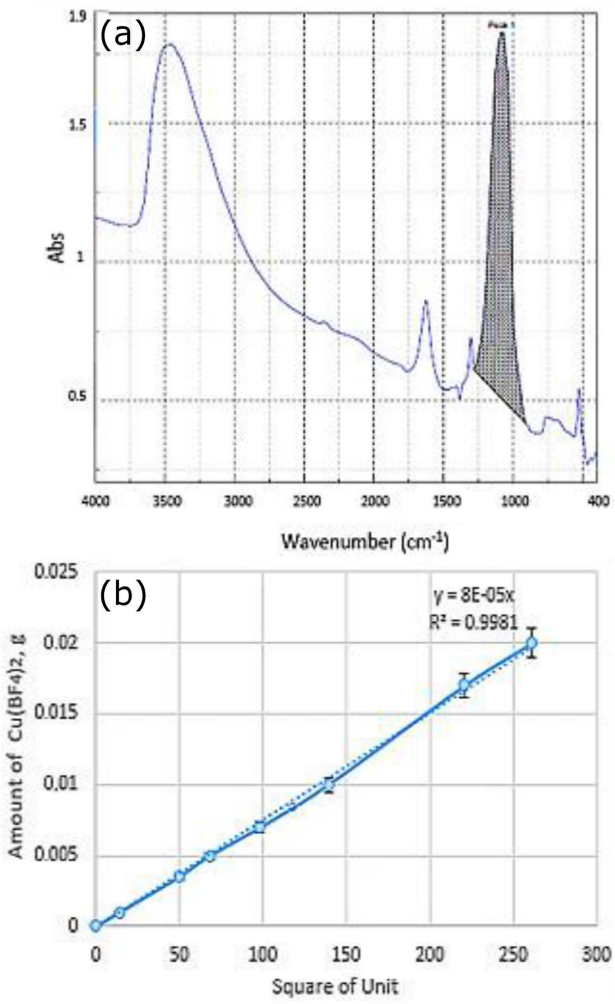

Fig. 1. (a) FTIR spectrum of commercial copper(II) fluoroborate, (b) the calibration curve of commercial copper(II) fluoroborate.

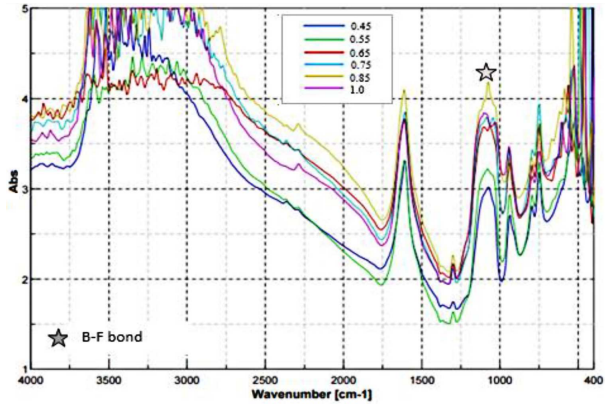

Fig. 2. FTIR spectra at different reactant mole ratio n_B/n_{CuF_2}.

The maximum yield was obtained at 0.85 mole ratio. It was seen that the yield decreased after reactant mole ratio of 0.85. It has been seen that BF_4^- ion selective electrode results support FTIR analysis results.

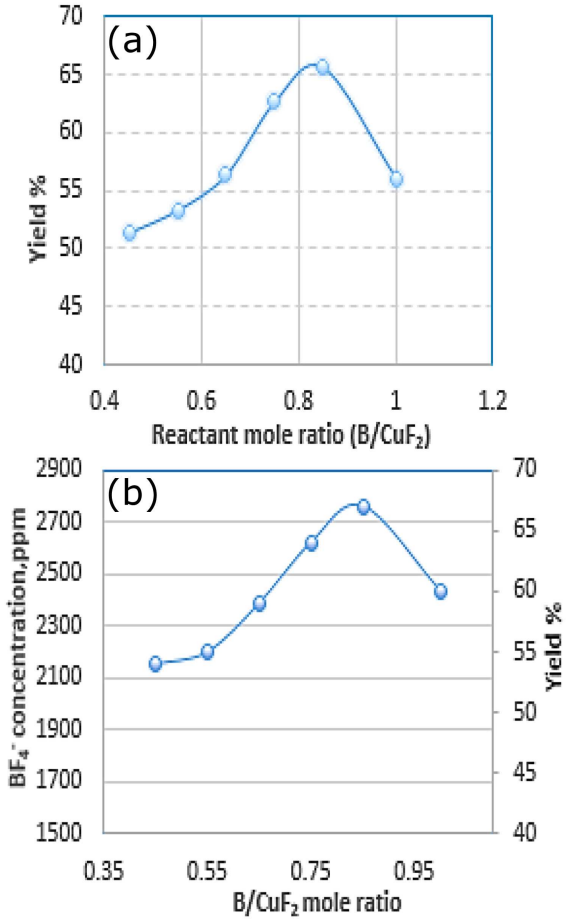

Fig. 3. (a) the effect of reactant mole ratio (B/CuF_2) on the product yield (FTIR analysis results), (b) BF_4^- concentration–yield graph at different mole ratio (BF_4^- ion selective electrode results).

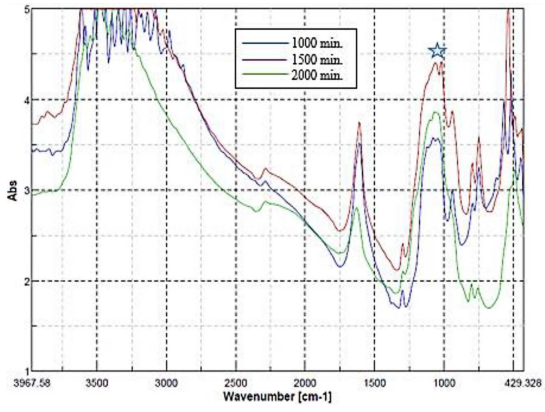

Fig. 4. FTIR peaks at different reaction periods (range of 1000–2000 min.

Optimum mole ratio was fixed for other experiments. The reaction periods were changed from 1000 to 2000 minutes. FTIR spectrums of the samples prepared at different reaction periods were given in Fig 4. Figure 4 indicates that the highest peak area was found when the reaction period was 1500 minutes.

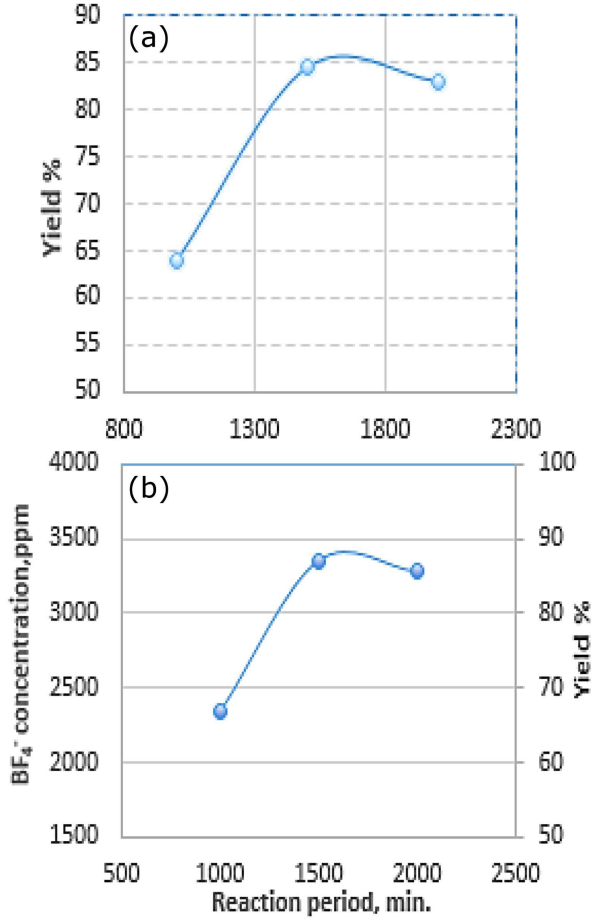

Fig. 5. (a) the effect of reaction period on the product yield (FTIR analysis results) (b) BF_4^- concentration–yield graph at different reaction periods (BF_4^- ion selective electrode results).

The yields which were found by using B–F bond FTIR peak area for different reaction periods (1000–2000) were given in Fig. 5a. The yield was increased from 1000 minutes to 1500 minutes. When the period was 1500 min, the yield was found as 84.5%. A significant increase was not observed at peak area when the reaction time was 2000 minutes. Longer milling duration provides smaller particle sizes and more homogeneous dispersion [14]. However, if the sample has been milled longer than necessary, the level of contamination increases and some unwanted phases form [15]. For this reason, the reactants must be milled with the optimum reaction period. The solutions of copper(II) fluoroborate samples obtained at the end of the different reaction periods were analyzed by ion selective electrode. The BF_4^- ion concentrations and yields obtained at different reaction periods were given in Fig 5b. As shown in Fig. 5b, the highest yield was obtained when the reaction time was 1500 minutes.

There is a small difference between the FTIR calibration graph and the BF_4^- ion selective electrode. This difference is 3%. It can be explained that FTIR calibration graph is considered to be more reliable method.

Synthetic copper(II) fluoroborate sample was tried to analyze by XRD instrument. But, it has been decomposed during the XRD analysis. There is no XRD pattern of copper(II) fluoroborate in the literature and instrument software.

4. Conclusion

In the study, copper fluoride and elemental boron were used as reactants for producing of copper(II) fluoroborate by ball milling method. A study on copper(II) fluoroborate synthesis by mechanochemical method with ball milling is not available in the literature so it is a new synthesis method to produce copper(II) fluoroborate. This synthesis method is feasible, simple and eco-friendly. Optimum conditions of reactant mole ratio and the reaction time were determined. A strong vibration peak corresponding to the B–F bond was apparent in FTIR analysis. Qualitative and quantitative analysis of product were performed using the FTIR spectroscopy. The results were supported by BF_4^- electrode. The optimum mole ratio (n_B/n_{CuF_2}) was found to be 0.85:1. The yield of copper(II) fluoroborate increased to reach the optimum mole ratio, but it was observed a decrease in yield after the optimum mole ratio. The reason is that the increase of the excess reactant causes dilution in the medium. After the determination of the optimum mole ratio, the optimum ball milling time was determined. It was seen that the increase in the period of staying in the ball mill had a positive effect on the yield. However, after reaching the ideal stage, there was no significant change in the yield with the increase of the reaction time. The optimum reaction period was found to be 1500 minutes. Copper(II) fluoroborate was successfully synthesized with 84.5% yield in the study at optimum conditions.

Acknowledgments

This work was supported by Eti Mine Works General Managements under Project Number 2014.C.11.0010.15. The authors are grateful to Eti Mine Works of Turkey for financial support and Gazi University for laboratory facilities usage.

References

[1] J.R. Papcun, *Fluorine Compounds, Inorganic, Fluoroboric Acid and Fluoroborates*, Wiley, New York 2000.

[2] A.V. Topchiev, S.V. Zavgorodnii, Y.M. Paushkin, W. Doering, D.H. Barton, *Boron Fluoride and Its Compounds as Catalysts in Organic Chemistry*, Pergamon Press, London 1959.

[3] S.K. Garg, R. Kumar, A.S. Chakraborti, *Tetr. Lett.* **46**, 1721 (2005).

[4] A. Wagh, Y. Raviprakash, S.D. Kamath, *J. All. Comp.* **695**, 2781 (2016).

[5] S.S. Zhang, K. Xu, T.R. Jow, *J. Electrochem. Soc.* **149**, 586 (2002).

[6] C.A. Wilkie, A.B. Morgan, *Fire Retardancy of Polymeric Materials*, CRC Press, Boca Raton 2009.

[7] L.I. Fidell, B. Brook, Fire-resistant finish for textiles comprising zinc fluoroborate, Patent US 357734 (1971).

[8] C. Suryanarayana, *Prog. Mater. Sci.* **46**, 1 (2001).

[9] P. Leoni, M. Sommovigo, M. Pasqualli, S. Midollini, D. Braga, P. Sabatino, *Organometallic* **10**, 1038 (1991).

[10] D.E. Bugay, *Adv. Drug Deliv. Rev.* **48**, 43 (2001).

[11] H. Namduri, S. Nasrazadani, *Corros. Sci.* **50**, 2493 (2008).

[12] D.Y. Aydın, M. Gürü, D. İpek, D. Özyürek, *Arab J. Sc. Eng.* **42**, 4409 (2017).

[13] S.S.M. Hassan, M.A.F. Elmosalami, *Anal. Chem.* **325**, 178 (1986).

[14] C. Suryanarayana, *Intermet.* **3**, 153 (1995).

[15] S.D. House, J.J. Vajo, C. Ren, A.A. Rockett, I.M. Robertson, *Acta Mater.* **86**, 55 (2015).