

Synthesis of Zinc Fluoroborate by Wet Method and Its Application as a Flame Retardant for Cotton Fabrics

Duygu Yılmaz Aydın* and Metin Gürü**

* Department of Bioengineering, Faculty of Engineering and Natural Sciences, Malatya Turgut Ozal University, Malatya, Turkey

**Department of Chemical Engineering, Faculty of Engineering, Gazi University, Ankara, Turkey

*Corresponding Author: duygu.aydin@ozal.edu.tr

Submitted : 05-12-2020

Revised : 23-09-2021

Accepted : 07-10-2021

ABSTRACT

In this study, zinc fluoroborate was synthesized by wet method using fluoroboric acid and zinc oxide as reactants, and its usability as a flame retardant for cotton fabrics was investigated. The wet method is economical, green, efficient, and applicable on a large scale. The maximum yield was related to the variation of reactant ratio, temperature, reaction time, and stirring rate. The product was characterized using Fourier-transform infrared spectroscopy, BF₄⁻ ion-selective electrode, and X-ray diffraction. The maximum yield of 97% was achieved at the reactant mole ratio (nZnO/nHBF₄) of 1:3, temperature of 90 °C, and reaction time of 90 min. The purity of the synthesized product was 98%. Flame retardancy and high-temperature resistance effects of zinc fluoroborate on cotton fabrics were investigated using the limiting oxygen index (LOI) and high-temperature durability tests, respectively. Although the LOI value of the untreated original fabric was 16, this value increased to >55 upon impregnating the fabric with 50% zinc fluoroborate solution.

KEYWORDS: Zinc fluoroborate; Zinc oxide; Fluoroboric acid; Flame retardant

INTRODUCTION

The development of novel flame retardants is an important research topic. Many types of fire retardants, including phosphorus, silicon, boron, nitrogen, and other miscellaneous elements, have been developed and made commercially available. Flame retardants move in the vapor or condensed phase via chemical or physical mechanisms to interfere with combustion during heating, pyrolysis, ignition, or flame spreading (Lu and Hamerton, 2002). The flame-retardant property of boron compounds is related to the formation of a surface-protective coal layer that acts as a barrier to prevent carbon oxidation. An acceptable fire-retardant material used for the treatment of textile substrates must be nontoxic. For environmental reasons, the use of halogen-containing flame retardants should be reduced. Boron-containing flame retardants are cheaper and less toxic alternatives than traditional flame retardants, such as halogen-containing flame retardants (Lu and Hamerton, 2002). Boron compounds that are active in the condensed phase are an important family of inorganic additives with flame-retardant properties that are environmentally friendly when used as flame retardants (Dogan and Unlu, 2014; Wang *et al.*, 2010). They are also used in smoke suppression, promoting charring, and as multifunctional flame retardants, such as pigments in dyes (Ayar *et al.*, 2014).

Fluoroborates are special boron compounds that can be used as flame retardants. The first scientific study on fluoroborates, which are salts of tetrafluoroboric acid, was conducted by Berzelius (Booth and Martin, 1949). The compounds in this group include alkali metal tetrafluoroborates, ammonium tetrafluoroborates, and transition element tetrafluoroborates. Obtaining expensive special boron compounds from inexpensive boron sources is important for economic gains. Fluoroborates can be obtained using wet (Ceyhan *et al.*, 2020) and mechanochemical methods (Aydın *et al.*, 2017; Aydın *et al.*, 2019). Wet chemical synthesis involves chemical reactions in the solution phase using reactants under appropriate experimental conditions and is very efficient, simple, fast, highly controllable, scalable, and does not require purification steps. Metal fluoroborates are produced by the wet method from the reaction of fluoroboric acid and metal salts, or boric acid and hydrofluoric acid with metal salts (Papcun, 2000). Fluoroborates are commercially important in various industries. Main group metal, transition, and other heavy-metal fluoroborate salts and ammonium fluoroborates are used in different fields. Fluoroborates, especially zinc fluoroborate, are versatile and robust catalysts used in various organic reactions and transformations (Achilonu and Umesiobi, 2010; Sarkar *et al.*, 2015; Pujala *et al.*, 2011; Ranu *et al.*, 1999). Lithium fluoroborate is used as an electrolyte in lithium-sulfur batteries. The Li-ion cell using lithium-fluoroborate-based electrolyte is less moisture-sensitive and exhibits much better performance in high-temperature electrolytes (Zhang *et al.*, 2002). Tetramethylammonium tetrafluoroborate has been used in electrochemical double-layer capacitors (Park and Kim, 2017). Fluoroborates are also used in glasses (Rayappan and Marimuthu, 2013). Fluoroborate glasses made of elements such as zinc (Prajnashree *et al.*, 2013), lead (Wagh *et al.*, 2017), lithium (Ibrahim *et al.*, 2016), and sodium (Rayappan *et al.*, 2010) when used with rare-earth elements exhibit good physical properties and provide thermal stability against devitrification. Furthermore, fluoroborates of elements such as tin, lead, and methylimidazolium are used in electroplating baths (Liu and Pritzker, 2003; Chen *et al.*, 1999). Fluoroborates increase the flame resistance of a material and reduce smoke. They are used as flame retardants in synthetic fibers, polymers (Wilkie and Morgan, 2009), textile materials, (Fidell and Brook, 1971; Kasem and Richard, 1972), etc.

Some test methods such as thermogravimetric analysis, limiting oxygen index (LOI) test, the UL-94 test, and the cone calorimeter test have been used to evaluate the flammability of flame-retardant materials (Bourbigot *et al.*, 1999). In this study, the LOI test, which measures the minimum oxygen concentration required for a material to support combustion, was used as the flammability test.

The purpose of this study was to synthesize zinc fluoroborate by wet method under optimum conditions and investigate its performance against flames and high temperatures in cotton fabrics.

MATERIALS AND METHODS

Zinc oxide (99% pure, Sigma-Aldrich) and fluoroboric acid solution (50% pure, Acros Organics) were used as reactants to synthesize zinc fluoroborate. High-purity commercial zinc fluoroborate was purchased from Sigma-Aldrich (333875).

The experiments were performed at different mole ratios, temperatures, and stirring rates. Zinc fluoroborate crystals were obtained after filtration. The chemical reaction is shown in Eq. (1):



The fluoroborate ion concentration was determined by fluoroborate-ion-selective electrode. Ion meter (S220) and BF_4^- ion-selective electrode (DX287) were supplied from Mettler Toledo (Figure 1). Synthetic and commercial zinc fluoroborate samples were analyzed using an XRD instrument (Rigaku). The synthesized product was characterized using Fourier-transform infrared (FTIR) spectroscopy (Jasco FTIR-480).



Figure 1. Experimental setup

Zinc fluoroborate solutions were prepared at different concentrations (15%, 30%, and 50%) for flame retarding tests. These solutions were then impregnated into cotton fabrics. The fabrics remained in the solution for 12 h and dried in an atmospheric environment. An LOI instrument (Dynisco) was used for the flammability tests (Figure 2). The fabric properties are listed in Table 1.



Figure 2. Limiting oxygen index chamber

Table 1. Properties of fabric used in the experiments

Fiber type	100% cotton
Weaving type	2×2
Areal density (g/m ²)	437
Weft density (picks/cm)	15 pieces
Waft density (ends/cm)	23 pieces

A high-temperature laboratory furnace was used for high-temperature durability tests. Original fabric and 50% zinc fluoroborate solution-impregnated fabric stayed 1 h at 120 °C, 200 °C, and 250 °C.

RESULTS AND DISCUSSION

The progress of the reaction was monitored by measuring the fluoroborate ion concentration in the reaction medium. The experiments were conducted at various mole ratios and temperatures. The optimum reactant mole ratio (nHBF₄/nZnO) was determined using different reactant mole ratios (1:1, 2:1, 3:1, 4:1, and 5:1). At first, the temperature and stirring rate were fixed at 50 °C and 300 rpm, respectively. The reaction could not be completed when the mole ratio (nHBF₄/nZnO) was 1:1. Figure 3 shows that, when the reactant mole ratios were 3:1 and 4:1, the yields were similar. In other words, the amount of product formed did not change at the end of the reaction when the reactant mole ratios (nHBF₄/nZnO) were 3:1 and 4:1. Excess fluoroboric acid did not change the amount of product formed beyond a certain amount. Zinc fluoroborate was produced with 67% yield at 50 °C, reactant mole ratio (nHBF₄/nZnO) of 3:1, and stirring rate of 300 rpm.

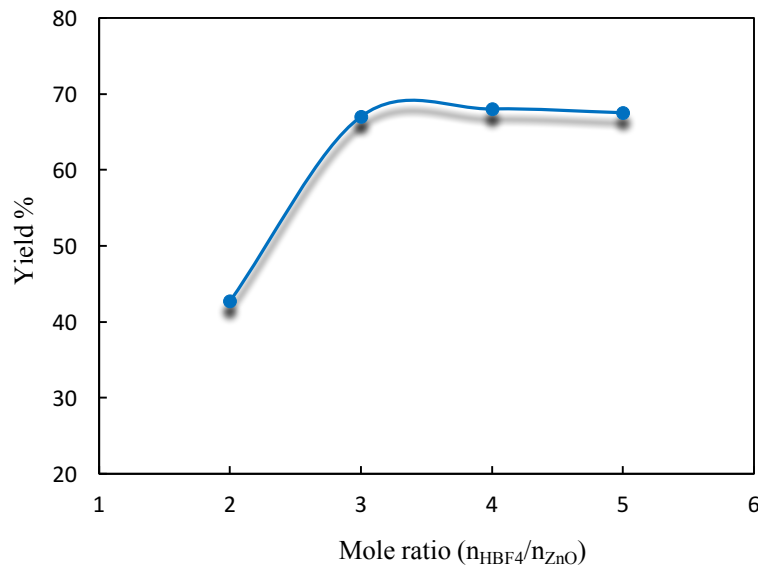


Figure 3. Effect of mole ratio (nHBF₄/ nZnO) on the product yield (50 °C, 300 rpm)

The experiments were performed at different temperatures (25 °C, 50 °C, 70 °C, 90 °C, and 98 °C) when the stirring rate was 300 rpm and mole ratio (nHBF₄/nZnO) was fixed at 3:1. The yield was determined based on the amount of product formed after the reaction was completed. The effect of temperature on the product yield is shown in Figure 4, which reveals that zinc fluoroborate production yield was enhanced when the temperature increased up to 90 °C. The amount of product formed was similar at 90 °C and 98 °C; thus, the yield is approximately the same at both temperatures. The yield was 97% at a reaction mole ratio (nHBF₄/nZnO) of 3:1,

temperature of 90 °C, reaction time of 90 min, and stirring rate of 300 rpm. Under optimum conditions, the speed range of the magnetic stirrer varied from 300 to 500 rpm, and the experiments were performed separately. The yield was unchanged and recorded as 97%. Synthetic and commercial zinc fluoroborate samples were analyzed using XRD and found to be decomposed. There is no XRD pattern of zinc fluoroborate in the literature or in the instrument software (Aydm *et al.*, 2019).

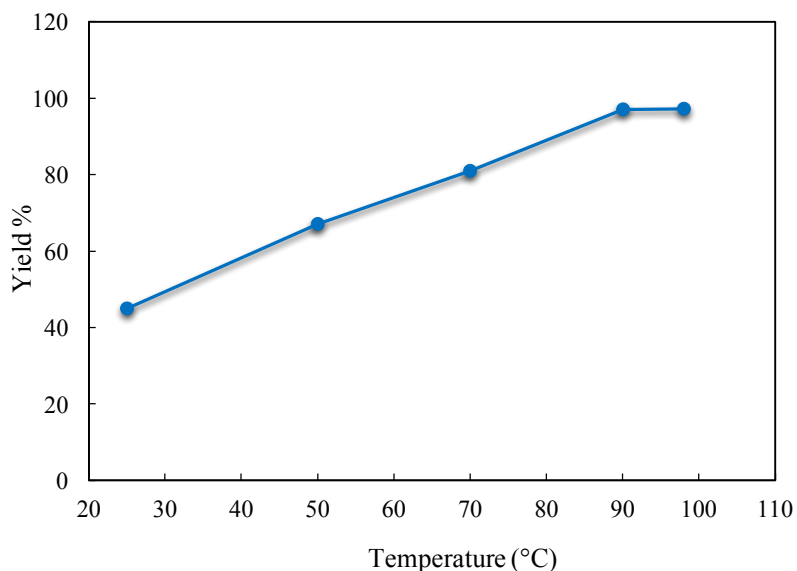


Figure 4. Effect of temperature on the product yield ($n_{\text{HBF}_4}/n_{\text{ZnO}}=3:1$, 90 min, 300 rpm)

The samples were taken from the reaction medium and diluted periodically at three different temperatures to determine the optimum reaction period. BF_4^- ion concentration was determined using ion-selective electrode. The time-dependent variation in the concentration is shown in Figure 5.

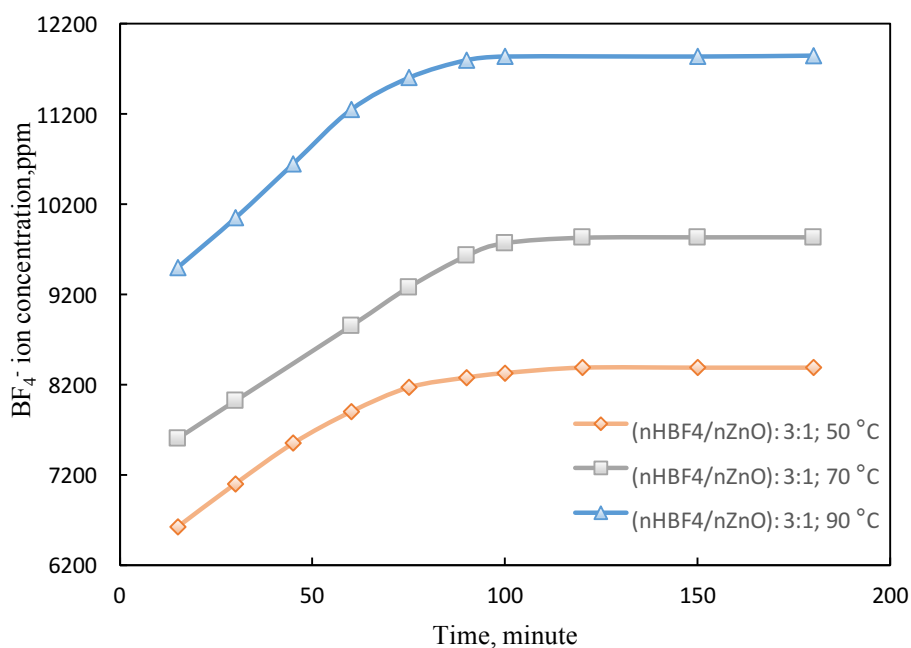


Figure 5. Change in BF_4^- ion concentration with time at different temperatures ($[n_{\text{HBF}_4}/n_{\text{ZnO}}]=3:1$, 90 min, 300 rpm)

Figure 5 shows that the fluoroborate ion concentration varied with temperature and reaction time. As temperature and time increased, the fluoroborate ion concentration in the reaction medium increased. After a certain amount of time, the fluoroborate ion concentration in the reaction medium was fixed. Figure 5 also illustrates that the fluoroborate ion concentration was fixed faster at 90 °C than at other operating temperatures. After 90 min, the concentration remained constant at 90 °C. A short reaction time may be selected if the reaction can be easily accomplished. The optimal reaction time was determined to be 90 min. Commercial and synthetic zinc fluoroborates were compared using FTIR spectroscopy. FTIR spectra of products synthesized at 90 °C and 98 °C and commercial zinc fluoroborate are shown in Figure 6. The characteristic FTIR absorption band of B-F is in the range of 1000 to 1100 cm^{-1} (Leoni *et al.*, 1991). Figure 6 shows that the FTIR peaks of the commercial and synthetic zinc fluoroborates overlap.

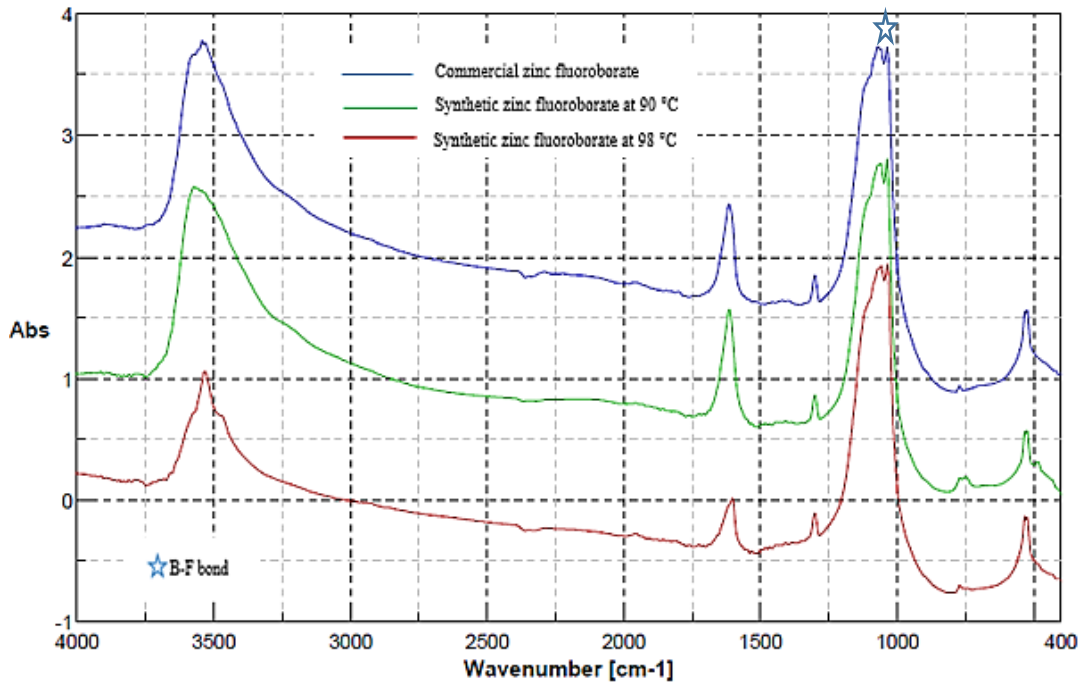


Figure 6. FTIR patterns of commercial zinc fluoroborate and synthetic zinc fluoroborate (produced at optimum conditions)

The purity of the product was determined using a calibration graph of commercial zinc fluoroborate. The solutions were prepared by using different amounts of commercial zinc fluoroborate. BF_4^- ion concentration of solutions was measured using BF_4^- ion-selective electrode. The calibration graph for zinc fluoroborate is shown in Figure 7.

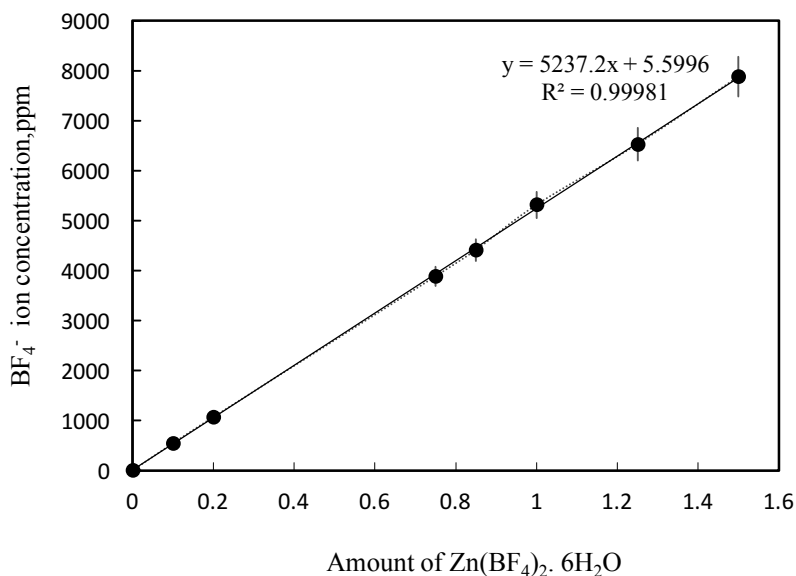


Figure 7. Calibration curve of commercial zinc fluoroborate

Zinc fluoroborate was synthesized at 98% purity under optimum conditions ($n_{\text{HBF}_4}/n_{\text{ZnO}} = 3:1$; 90 °C; 300 rpm; 90 min).

The flame retardancy of the samples was characterized using the LOI test. Atmospheric air contains approximately 21% oxygen. A material with an LOI value of <21 burns very easily, whereas the LOI value of a slow-burning material is expected to be >21% but <28%. A self-extinguishing material has LOI > 28% and stops burning after the ignition source has been removed. There is a relationship between LOI and the characteristics of the material, such as the heat dissipation rate, smoke density, and total heat release (Friedrich and Breuer, 2015). The LOI tests of impregnated fabrics with zinc fluoroborate solutions of 15%, 30%, and 50% were conducted according to the ASTM D2863 standard, and the results were compared with the LOI value of the original fabric. Impregnation of a flame-retardant solution is usually preferred to surface treatment because it penetrates below the surface to provide more effective protection, and its effect lasts longer (Tondi *et al.*, 2014). The fabrics used were of the same size and properties. The LOI values are listed in Table 2.

Table 2. LOI values of untreated and zinc fluoroborate-impregnated fabrics (at different concentrations)

Fluoroborate concentration, %	LOI, O ₂ %
Untreated fabric	16
15% solution-impregnated fabric	28
30% solution-impregnated fabric	45
50% solution-impregnated fabric	>55

The LOI value of 50% zinc fluoroborate solution-impregnated fabric was >55%. This value represents the maximum amount of oxygen for the LOI chamber instrument. A considerable increase in LOI was observed when the cotton fabric was impregnated with zinc fluoroborate, which indicates that the addition of zinc fluoroborate significantly improved the flame retardancy of cotton fabrics.

High-temperature durability tests revealed that cotton fabrics were resistant to high temperatures. The original untreated fabric and 50% zinc fluoroborate solution-impregnated fabric were both exposed to high temperatures (120 °C, 200 °C, and 250 °C). The images of the fabric samples at the end of the experiment are shown in Figure 8.

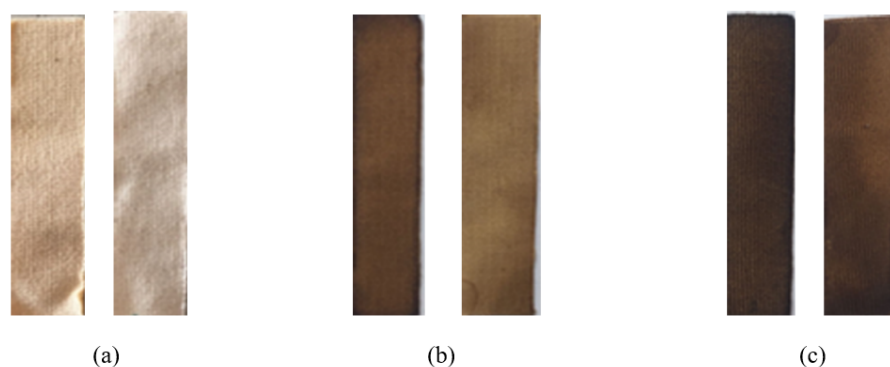


Figure 8. Images of untreated and zinc fluoroborate-impregnated fabrics after high-temperature durability tests (a) 120 °C (b) 200 °C (c) 250 °C

Figure 8 shows that the color of the fabric gradually changed from pale yellow to dark brown. In this test, the color change of the untreated fabric was greater than that of the zinc fluoroborate solution-impregnated fabric when exposed to high temperatures. Additionally, the zinc fluoroborate-impregnated fabric had better resistance to high temperatures than the untreated original fabric.

CONCLUSION

Zinc fluoroborate was synthesized by wet method, an economical process, using zinc oxide and fluoroboric acid, with 97% yield and 98% purity. We investigated the effects of reactant ratio, temperature, stirring rate, and reaction time on the yield. The maximum product yield was obtained at the reactant ratio ($n\text{ZnO}/n\text{HBF}_4$) of 1:3, temperature of 90 °C, reaction time of 90 mins, and stirring rate of 300 rpm. The flame-retardancy effect of zinc fluoroborate on cotton fabric was determined using LOI and high-temperature durability tests. The LOI value of zinc fluoroborate-impregnated fabric was found to be >55%. The color change of the original untreated fabric upon exposure to high temperatures was greater than that of the zinc fluoroborate-impregnated fabric. Zinc fluoroborate also enhanced the resistance of the cotton fabric to high temperatures. These results imply that zinc fluoroborate exhibits excellent flame retardancy for cotton fabrics and is a candidate for impressive flame retardant for cotton fabrics.

REFERENCES

- Achilonu, M.C. & Umesiobi, D.O. 2010.** The formation of carbon–carbon and carbon–heteroatom bonds using silver **tetrafluoroborate** as a promoter. *Arabian Journal of Chemistry*, **9**(2): 1984-2003
- Ayar, B., Gürü, M. & Çakanyıldırım, Ç. 2014.** Solid phase synthesis of anhydrous zinc borate from zinc and boron oxide and utilization as a flame **retardant** in dye and textile. *Gazi University Journal of Science*, **27**(3): 987-991.
- Aydın, Y.D., Gürü, M., İpek, D. & Özyürek, D. 2019.** Obtainment of copper(II) fluoroborate by high-energy impacted ball-milling. *Acta Physica Polonica A*, **135**: 888-891.
- Aydın, Y.D., Gürü, M., İpek, D. & Özyürek D. 2017.** Synthesis and characterization of zinc fluoroborate from zinc fluoride and boron by mechanochemical reaction. *Arabian Journal of Science and Engineering*, **42**: 4409-4416.
- Booth, H.S. & Martin, D.R. 1949.** Boron Trifluoride and Its Derivatives, Wiley, Newyork.

- Bourbigot, S., Bras, M.L., Leeuwendal, R., Shenc, K.K. & Schubert, D. 1999.** Recent advances in the use of zinc borates in flame retardancy of EVA. *Polymer Degradation and Stability*, **64**(3): 419-425.
- Ceyhan, A.A., Bağcı, S., Baytar O., & Şahin Ö. 2020.** Ammonium fluoroborate production and determination of production parameters. *Journal of Boron*, **5**(2): 63-72
- Chen, P.Y. & Sun, I.W. 1999.** Electrochemical study of copper in a basic 1-ethyl-3 methylimidazolium tetrafluoroborate room temperature molten salt. *Electrochimica Acta*, **45**(3): 441-450.
- Dogan, M. & Unlu, M. 2014.** Flame retardant effect of boron compounds on red phosphorus containing epoxy resins. *Polymer Degradation and Stability*, **99**(2014): 12-17.
- Fidell, L.I. & Brook, B. 1971.** Fire-resistant finish for textiles comprising zinc fluoroborate, Patent US 357734.
- Friedrich, K. & Breuer, U. 2015.** Multifunctionality of polymer composites: challenges and new solutions. Elsevier, United States of America.
- Ibrahim, S., Elbatal, F.H. & Abdelghany, A. 2016.** Optical character enrichment of NdF₃-doped lithium fluoroborate glasses. *Journal of Non-Crystalline Solids*, **453**: 16-22.
- Kasem, M.A. & Richard, H.R. 1972.** Flame-retardants for fabrics- function of boron-containing additives. *Industrial & Engineering Chemistry Product Research and Development*, **11**(2): 114-133.
- Leoni, P., Sommovigo, M., Pasqualli, M., Midollini, S., Braga, D. & Sabatino, P. 1991.** Coordinated water/anion hydrogen bonds and Pd-H bond acidity in cationic palladium(II) aquo hydrides and the x-ray crystal and molecular structures of trans- [(Cy₃P)₂Pd(H)(H₂O)]BF₄ (Cy = cyclohexyl). *Organometallics*. **10**(4): 1038-1044.
- Liu, Y. & Pritzker, M. 2003.** Effect of pulse plating on composition of Sn-Pb coatings deposited in fluoroborate solutions. *Journal of Applied Electrochemistry*, **33**(12): 1143-1153.
- Lu, S.Y. & Hamerton, I. 2002.** Recent developments in the chemistry of halogen-free flame retardant polymers. *Progress in Polymer Science*, **27**(8): 1661-1712.
- Papcun, J.R. 2000.** Fluorine compounds, inorganic, fluoroboric acid and fluoroborates. "In: Kirk-Othmer Encyclopedia of Chemical Technology, Wiley, New York.
- Park, S. & Kim, K. 2017.** Tetramethylammonium tetrafluoroborate: The smallest quaternary ammonium tetrafluoroborate salt for use in electrochemical double layer capacitors. *Journal of Power Sources*, **338**: 129-135.
- Prajnashree, M., Wagh, A., Sangeetha, B. & Kamath, D.S. 2013.** Characterization of Pr₆O₁₁ doped zinc fluoroborate glass. *European Scientific Journal*, **9**(18): 83-92.
- Pujala, B., Rana, S. & Chakraborti, A.K. 2011.** Zinc tetrafluoroborate hydrate as a mild catalyst for epoxide ring opening with amines: scope and limitations of metal tetrafluoroborates and applications in the synthesis of antihypertensive drugs (RS)/(R)/(S)-metoprolols. *The Journal of Organic Chemistry*, **76**(21): 8768-878.
- Ranu, B.C., Jana, U. & Majee, A. 1999.** A simple and efficient method for selective deprotection of t-butyl dimethylsilyl ethers by zinc tetrafluoroborate in water. *Tetrahedron Letters*, **40**(10): 1985-1988.
- Rayappan, I.A. & Marimuthu, K. 2013.** Structural and luminescence behavior of the Er³⁺ doped alkali fluoroborate glasses. *Journal of Non-Crystalline Solids*, **367**: 43-50.
- Rayappan, I.A., Marimuthu, K., Babu, S.S. & Sivaraman, M. 2010.** Concentration dependent structural, optical and thermal investigations of Dy³⁺-doped sodium fluoroborate glasses. *Journal of Luminescence*, **130**(12): 2407-2412.

Sarkar, A., Santra, S., Kundu, S.K., Ghosal, N.C., Hajra, A. & Majee, A. 2015. Zinc tetrafluoroborate: a versatile and robust catalyst for various organic reactions and transformations. *Synthesis*, **47**: 1379-1386.

Tondi, G., Haurie, L., Wieland, S., Petutschnigg, A., Lacasta, A., Monton, J. 2014. Comparison of disodium octaborate tetrahydrate-based and tanninboron- based formulations as fire retardant for wood structures. *Fire and Materials*, **38**(3): 381–390.

Wagh, A., Raviprakash, Y. & Kamath, S.D. 2017. Gamma rays interactions with Eu_2O_3 doped lead fluoroborate glasses. *Journal of Alloys and Compounds*, **695**: 2781-2798.

Wang, X., Song, Y. & Bao, J. 2010. Synergistic effects of ZrO_2 or B_2O_3 on flame-retarded poly (butyl methacrylate) with tricresylphosphate. *Fire and Materials*, **34**(7): 357-366.

Wilkie, C.A. & Morgan, A.B. 2009. Fire retardancy of polymeric materials. 2nd ed., CRC Press, Boca Raton.

Zhang, S.S.; Xu, K. & Jow, T.R. 2002. Study of LiBF_4 as an electrolyte salt for a li-ion battery. *Journal of The Electrochemical Society*, **149**(5): A586–A590.