# Combined Hydrothermal Synthesis of Zinc and Magnesium Borates at 100$^{o}$C Using ZnO, MgO and $H_3BO_3$

N. Tugrul, A. S. Kipcak, N. Baran Acarali, E. Moroydor Derun, S. Piskin



***Abstract*****—**Magnesium borate(MB) istechnical ceramic for high heat-resisting, corrosion-resisting, super mechanical strength, superinsulation, light weight, high strength, and high coefficient of elasticity. Zinc borate (ZB) can be used as multi-functional synergistic additives with flame retardant additives in polymers. The most important properties are low solubility in water and high dehydration temperature. ZB dehydrates above 290°C and anhydrous ZB has thermal resistance about 400°C. In this study, the raw materials of ZnO, MgO and $H_3BO_3$ were used with mole ratio of 1:1:9. With the starting materials hydrothermal method was applied at a temperature of 100$^{o}$C. The reaction time was determined as 30, 60, 90 and 120 minutes after some preliminary experiments. After the synthesis, the crystal structure and the morphology of the products were examined by X-Ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FT-IR). As a result, the forms of Zinc Oxide Borate Hydrate [$Zn_3B_6O_{12}.3.5H_2O$], Admontite [$MgO(B_2O_3)_3.7(H_2O)$] and Mcallisterite [$Mg_2(B_6O_7(OH)_6)_2.9(H_2O)$] were synthesized.

***Keywords*****—**Magnesium borate, zinc borate, XRD, FT-IR.

## I. Introduction

SINGLE-CRYSTALLINE magnesium borate $Mg_2B_2O_5$ nanorods have been synthesized via a simple route based on the calcinations of mixed powders containing $Mg(OH)_2$ and $H_3BO_3$at 900$^{o}$C in 3h. The nanorods have the typical diameters in the range of 70–120nm and the lengths up to a few micrometers [1]. Single-phase $Mg_3B_2O_6$ and $Mg_2B_2O_5$ ceramics have synthesized from MgO and $B_2O_3$ using solid-state reaction techniques. At the end of the experiments $Mg_2B_2O_5$ forms 1250-1280$^{o}$C temperature range and $Mg_3B_2O_6$forms 1200-1300$^{o}$C temperature range [2]. B and MgO (with a molar ratio of 1:1) have thoroughly mixed to prepare $Mg_3B_2O_6$nanobelts. Under flowing mixed Ar/$H_2O$ gases, the mixture of B and MgO was heated to 1100$^{o}$C and held at this temperature for 90min, and then subsequently cooled to room temperature [3]. Using $MgCl_2.6H_2O$ and $NaBH_4$ powders as the starting materials for the production of monoclinic $Mg_2B_2O_5$, the mixture was firstly milled for 120 h, and then sintered at 800°C for 2h. It was seen that mechanic process needed to formation of Mg-B-H [4]. Zinc borate is an important inorganic hydrated borate that finds applications ranging from polymers to paints for various purposes, such as flame retardant, corrosion inhibitor, etc. depending on the type of zinc borate [5]. Zinc borate is a multifunctional fire retardant containing different proportion of zinc and boric oxides [6]. Zinc borate are widely used in plastic, rubber, ceramics, paint, wire, electrical insulation, wood applications, cement and pharmaceutical industries due to its properties [7], [8].The production of $2ZnO·3B_2O_3·3H_2O$ from zinc oxide and boric acid via a rheological phase reaction was studied by Shi et al. [9]. The characterizations of the products were done by XRD, TG, DTA and SEM. Addition; the effects of experimental conditions and particle size distribution on the characteristics of the products were investigated. This synthetic method is green, and without pollution it provides a yield of approximately 100%.

In this study, combined hydrothermal synthesis of zinc and magnesium borates at 100$^{o}$C using ZnO, MgO and $H_3BO_3$ is aimed. Synthesized products are characterized by X-Ray Diffraction (XRD) (Philips PANalytical, Xpert-Pro) and Fourier Transform Infrared Spectroscopy (FT-IR) (Perkin Elmer, Spectrum One).

## II. Materials and Methods

### *A. Raw Material Preparation*

Zinc oxide was supplied from Colakoglu Chemistry Limited Company, magnesium oxide was supplied from merck chemicals and boric acid was retrieved from Kirka Boron Management Plant in Eskisehir. Zinc oxide and magnesium oxide were used without pretreatment and boric acid was crushed, grinded with agate mortar and sieved to 200 meshes (Fig. 1). Identification analysis of zinc oxide, magnesium oxide and boric acid were made by Philips PANalytical X-Ray Diffraction that can be seen in Fig. 2.

Addition to the XRD analysis, Perkin Elmer Brand Fourier Transform Infrared Spectroscopy (FT-IR) technique with Universal ATR sampling accessory – Diamond / ZnSe Crystal

N. Tugrul is with the Yildiz Technical University, Department of Chemical Engineering, Davutpasa Campus, 34210 Esenler, Istanbul, Turkey (phone: 0090-212-3834776; fax: 0090-212-3834725; e-mail: ntugrul@hotmail.com).

A. S. Kipcak is with the Yildiz Technical University, Department of Chemical Engineering, Davutpasa Campus, 34210 Esenler, Istanbul, Turkey (phone: 0090-212-3834751; fax: 0090-212-3834725; e-mail: skipcak@ yildiz.edu.tr).

N. BaranAcarali is with the Yildiz Technical University, Department of Chemical Engineering, Davutpasa Campus, 34210 Esenler, Istanbul, Turkey (phone: 0090-212-3834766; fax: 0090-212-3834725; e-mail: nbaran@ yildiz.edu.tr).

E. Moroydor Derun is with the Yildiz Technical University, Department of Chemical Engineering, Davutpasa Campus, 34210 Esenler, Istanbul, Turkey (e-mail: moroydor@yildiz.edu.tr).

S. Piskin is with the Yildiz Technical University, Department of Chemical Engineering, Davutpasa Campus, 34210 Esenler, Istanbul, Turkey (e-mail: piskin@yildiz.edu.tr).

was used. Measurement range was selected as 4000–650 $cm^{-1}$, scan number was 4 and resolution set as 4 $cm^{-1}$(Fig. 3).

(a) (b)

Fig. 1 (a) Agate mortar, (b) Sieve

Fig. 2 Philips PANalytical X-Ray Diffraction

Fig. 3 Perkin Elmer Spectrum One FT-IR Spectrometer

### *B. Combined Hydrothermal Synthesis*

For synthesis, mole ratio of zinc oxide, magnesium oxide and boric acid was determined experimentally and found as 1:1:9. The liquid phase was used as demineralized water (18.3 mΩ.cm) that produced from the equipment of Human Power I+ Water Purification System.

Experiment temperature was selected as 100°C, and four different reaction times were conducted to investigate the phase transition between different types of zinc borates and magnesium borates according to the reaction time changes. The reaction intervals were set to 30, 60, 90 and 120 minutes. In synthesis procedure, firstly boric acid was dissolved in water at the desired temperature, then zinc oxide and zinc borate retrieved from local market in Turkey (in terms of boric acid, 0.5% w/w) was added, after the determined interval magnesium oxide was added to the mixture. So, reaction times were come up as 60, 120, 180 and 240 minutes for zinc borates and reaction times were come up as 30, 60, 90 and 120 minutes for magnesium borates.

### *C. Characterization of the Products*

All products were characterized by XRD (Philips Panalytical, Xpert-Pro). Furthermore, FT-IR (Perkin Elmer, Spectrum One) was used to identify the functional groups present in the products.

## Results and Discussion

### *A. Raw Material Characterization*

XRD analysis results of raw materials were given in Figs. 4-6 and Table I.

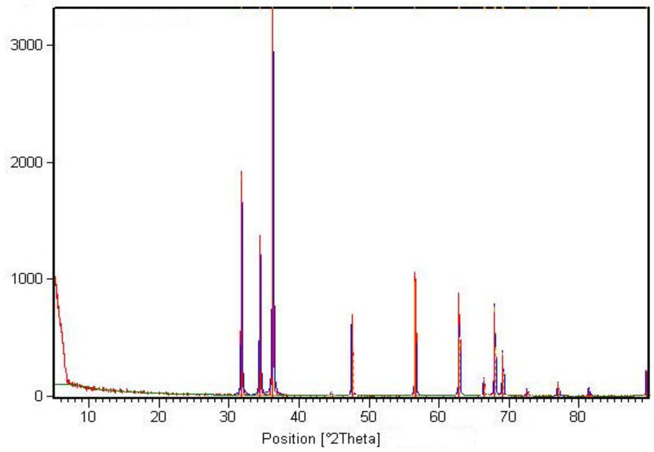


Fig. 4 XRD pattern of ZnO

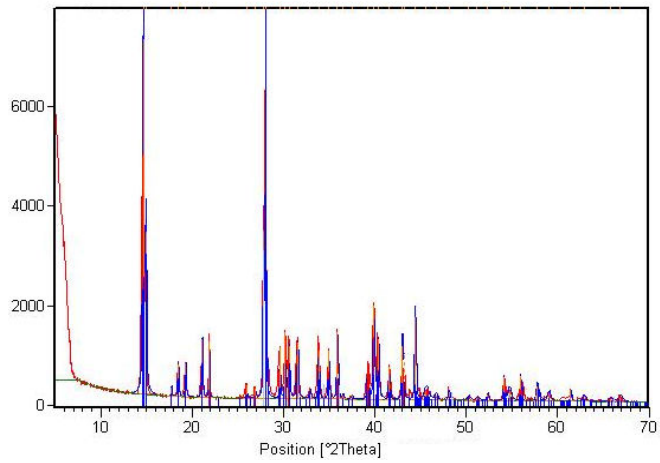


Fig. 5 XRD pattern of boric acid

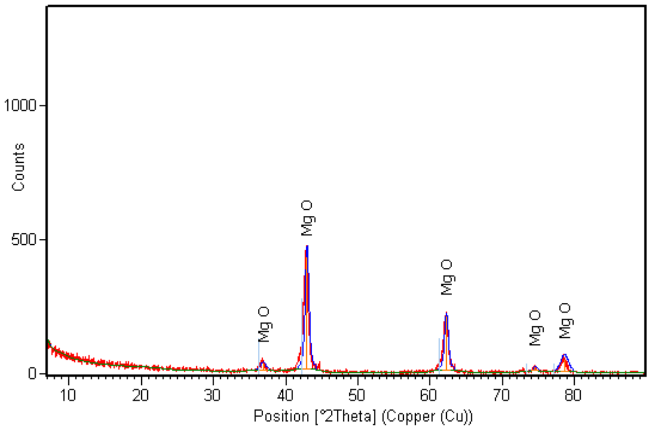


Fig. 6 XRD pattern of MgO

TABLE I
XRD RESULTS OF REACTIVES

| Reference Code | Compound Name | Chemical Formula | Score |
|---|---|---|---|
| 01-079-2205 | Zinc oxide | $ZnO$ | 91 |
| 01-073-2158 | Sassolite | $H_3BO_3$ | 62 |
| 01-087-0651 | Periclase | $MgO$ | 78 |

From the results of the XRD analysis “01-079-2205” coded zinc oxide ($ZnO$), “01-073-2158” coded sassolite ($H_3BO_3$) and “01-087-0651” coded periclase ($MgO$) were found.

FT-IR spectrums of zinc oxide, magnesium oxide and boric acid were given in Figs. 7 and 8.

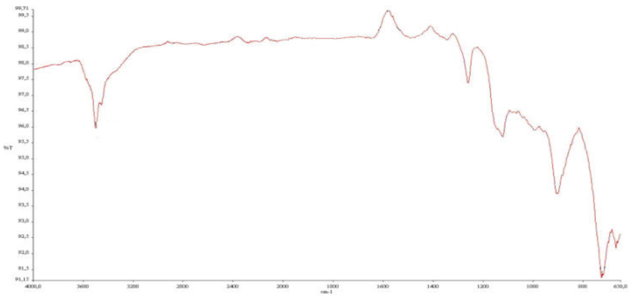

Fig. 7 FT-IRspectra of ZnO

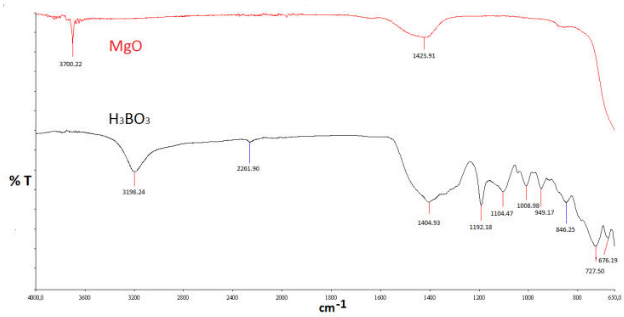


Fig. 8 FT-IR spectrum of magnesium oxide and boric acid

*B. XRD Results*

The XRD results of the synthesized zinc borates and magnesium borates at 100°C were given in Tables II and III, respectively.

TABLE II
XRD RESULTS OF ZINC BORATES SYNTHESIZED AT 100°C

| Reaction Time (mins) | pdfno | Name | Formula | Score |
|---|---|---|---|---|
| 60 | 00-011-0279 | Zinc Borate Hydrate | $Zn_2B_6O_{11}.7H_2O$ | 17 |
| | 00-032-1461 | Zinc Borate Hydrate | $Zn_3B_{10}O_{18}.14H_2O$ | 41 |
| | 01-075-0766 | Zinc Borate Hydroxide Hydrate | $Zn(B_3O_3(OH)_5).H_2O$ | 32 |
| | 00-021-1474 | Zinc Borate Hydrate | $Zn_6B_{10}O_{11}.3H_2O$ | 9 |
| | 00-035-0433 | Zinc Oxide Borate Hydrate | $Zn_3B_6O_{12}.3.5H_2O$ | 22 |
| 120 | 00-035-0433 | Zinc Oxide Borate Hydrate | $Zn_3B_6O_{12}.3.5H_2O$ | 75 |
| 180 | 00-035-0433 | Zinc Oxide Borate Hydrate | $Zn_3B_6O_{12}.3.5H_2O$ | 78 |
| 240 | 00-035-0433 | Zinc Oxide Borate Hydrate | $Zn_3B_6O_{12}.3.5H_2O$ | 76 |

Five different zinc borates were formed at the reaction time of 60 minutes. After the reaction time of 60 minutes, the expected formation of zinc borate of “00-035-0433” zinc oxide borate hydrate ($Zn_3B_6O_{12}.3.5H_2O$) was formed. The highest zinc borate XRD crystal score was obtained at the reaction time of 180 minutes. The XRD patterns of the zinc borates were shown in Fig. 9.

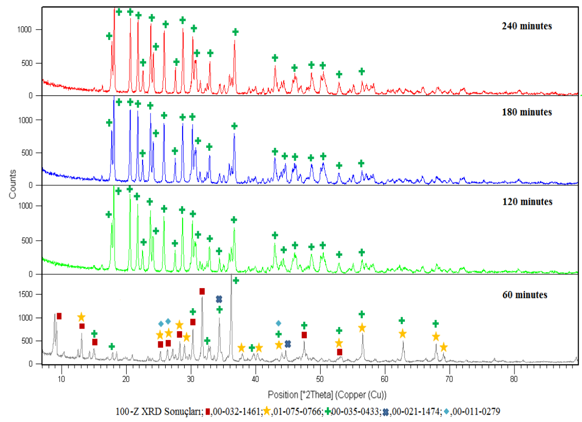


Fig. 9 XRD patterns of zinc borates synthesized at 100°C;
00-011-0279: 00-032-1461: 01-075-0766:
00-021-1474: 00-035-0433:

TABLE III
XRD RESULTS OF MAGNESIUM BORATES SYNTHESIZED AT 100°C

| Reaction Time(mins) | pdfno | Name | Formula | Score |
|---|---|---|---|---|
| 30 | 01-070-1902 | Mcallisterite | $Mg_2(B_6O_7(OH)_6)_2.9(H_2O)$ | 84 |
| | 01-076-0540 | Admontite | $MgO(B_2O_3)_3.7(H_2O)$ | 9 |
| 60 | 01-070-1902 | Mcallisterite | $Mg_2(B_6O_7(OH)_6)_2.9(H_2O)$ | 89 |
| | 01-076-0540 | Admontite | $MgO(B_2O_3)_3.7(H_2O)$ | 15 |
| 120 | 01-070-1902 | Mcallisterite | $Mg_2(B_6O_7(OH)_6)_2.9(H_2O)$ | 85 |
| | 01-076-0540 | Admontite | $MgO(B_2O_3)_3.7(H_2O)$ | 49 |
| 180 | 01-070-1902 | Mcallisterite | $Mg_2(B_6O_7(OH)_6)_2.9(H_2O)$ | 83 |
| | 01-076-0540 | Admontite | $MgO(B_2O_3)_3.7(H_2O)$ | 64 |

From the XRD results it was seen that two types of magnesium borates were formed namely mcallisterite and admontite. These two formations were seen at all the reaction times. The highest mcallisterite and admontite formations were seen on 60 and 180 minutes of reaction times, respectively. The XRD patterns of the magnesium borates synthesized at 100°C were shown in Fig. 10.

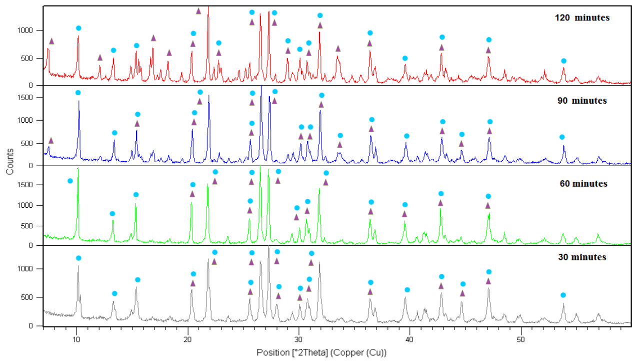


Fig. 10 XRD patterns of magnesium borates synthesized at 100°C; 01-070-1902: ● 01-076-0540: ▲

*C. FT-IR Results*

The FT-IR spectrums and peak interpretations of the synthesized zinc borates and magnesium borates at 100°C were given in Figs. 11, 12 and Table IV, respectively.

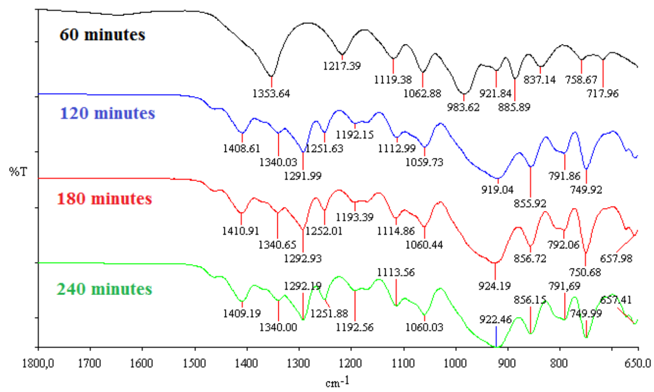


Fig. 11 FT-IR spectrum of zinc borates synthesized at 100°C

At the FT-IR spectrums of zinc borates the peaks at 1400cm$^{-1}$ represents the three coordinate boron asymmetrical stretching, the peaks between 1323 and 1217cm$^{-1}$, represents the OH$^{-1}$ in plane stretching due to the crystal waters inside the zinc borates. Four coordinate boron asymmetrical stretching was observed between the peaks of 1119 and 983cm$^{-1}$. Three coordinate boron symmetrical stretching was obtained at the peaks between 920 and 837cm$^{-1}$. The last peaks between the 790 and 657cm$^{-1}$, were the stretching of three coordinate boron.

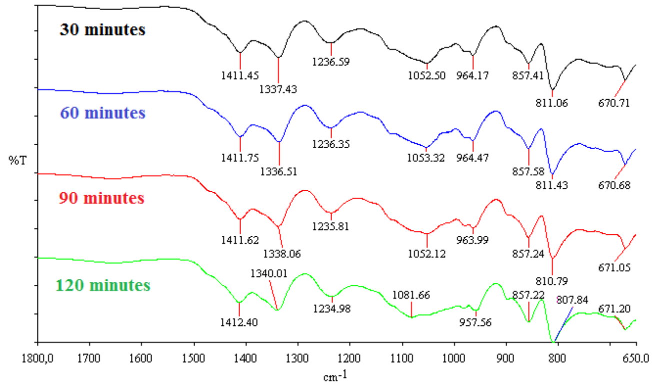


Fig. 12 FT-IRspectrum of magnesium borates synthesized at 100°C

In magnesium borates FT-IR spectrums similar to zinc borate spectrums at around 1400cm$^{-1}$ represents the three coordinate boron asymmetrical stretching. Other two peaks at around 1337 and 1235cm$^{-1}$, was OH$^{-1}$ in plane stretching due to the crystal waters inside the magnesium borates. The peaks between 1040 and 857cm$^{-1}$ represents four coordinate boron asymmetrical stretching. Also in magnesium borates OH$^{-1}$ out of plane stretching was seen addition to zinc borates which it was due to the crystal waters inside the magnesium borates also like OH$^{-1}$ in plane stretching. The last peak represents the stretching of three coordinate boron with the peaks values at around 670cm$^{-1}$.

TABLE IV
FT-IR PEAK INTERPRETATIONS

| Peaks (cm$^{-1}$) | Peak Interpretation |
|---|---|
| 1600-1400 | $B_3$-O asymmetrical stretching |
| 1400-1200 | OH$^{-1}$ in plane stretching |
| 1200-950 | $B_4$-O asymmetrical stretching |
| 950-850 | $B_3$-O symmetrical stretching |
| 850-750 | OH$^{-1}$ out of plane stretching |
| 750-650 | $B_3$-O stretching |

## III. CONCLUSION

Zinc borates (ZB) and Magnesium borates (MB) are multifunctional fire retardants containing different proportion of zinc, magnesium and boric oxides, respectively. The analysis results (XRD and FT-IR) showed that combined hydrothermal synthesis of zinc and magnesium borates at 100°C using ZnO, MgO and $H_3BO_3$ was achieved.

The best XRD crystal results were obtained 180 and 120 minutes reaction time for zinc borates and magnesium borates respectively. For the combined hydrothermal synthesis of both zinc and magnesium borates either 120 or 180 minutes of reaction time was seen optimum values. The selected ratio of raw materials $ZnO:MgO:H_3BO_3$ (1:1:9 or 3:3:27) was also perfectly fit with the expected two step reaction and one step washing process given in (1) between (3).

*Step 1*

$$3ZnO + 27H_3BO_3 + aH_2O \rightarrow Zn_3B_6O_{12}.3.5H_2O + 21H_3BO_3 + bH_2O \quad (1)$$

where zinc borate was obtained at crystal phase

*Step 2*

$$3MgO + 21H_3BO_3 + cH_2O \rightarrow$$
$$dMgO(B_2O_3)_3.7(H_2O) + (3-d)Mg_2(B_6O_7(OH)_6)_2.9(H_2O) + 3H_3BO_3 + eH_2O \quad (2)$$

where magnesium borates were obtained at the solution phase and crystallized at 40$^o$C.

*Step 3 (Washing process)*

$$dMgO(B_2O_3)_3.7(H_2O) + (3-d)Mg_2(B_6O_7(OH)_6)_2.9(H_2O) + 3H_3BO_3 \rightarrow$$
$$dMgO(B_2O_3)_3.7(H_2O) + (3-d)Mg_2(B_6O_7(OH)_6)_2.9(H_2O) \quad (3)$$

where in this step, excess boric acid was removed from the crystal phase.

From the FT-IR spectrums of the zinc and magnesium borates synthesized by combined hydrothermal method, it was seen that at all the reaction times the zinc and magnesium borates were obtained. At the formation of zinc borates the different formation was seen on the 60 minutes of reaction time in XRD results, also this different formation was also seen in the FT-IR results, since some peaks were differ from the other spectrums.

## REFERENCES


[1] E.M. Elssfah, A. Elsanousi, J. Zhang, H.S. Song, and C.Tang, “Synthesis of magnesium borate nanorods”, *Mater. Lett.,* vol. 61pp. 4358–4361, 2007.

[2] U. Dosler, M. M. Krzmanc, and D. Suvorov, “The synthesis and microwave dielectric properties of $Mg_3B_2O_6$and$Mg_2B_2O_5$ceramics”, *J. Eur. Ceram. Soc.,*vol.30, pp. 413–418, 2010.

[3] J. Zhang, Z. Li, and B. Zhang, “Formation and structure of single crystalline magnesium borate ($Mg_3B_2O_6$) nanobelts”, *Mater. Chem. Phys.,* vol. 98, 195–197, 2006.

[4] S. Li, X. Fang, J.Leng, H.Shen, Y. Fan, and D.Xu, “A new route for the synthesis of $Mg_2B_2O_5$ nanorods by mechano-chemical and sintering process”, *Mater. Lett.,* vol. 64, pp. 151–153, 2010.

[5] M. Gonen, D. Balkose, R. B. Gupta, and S. Ulku, “Supercritical carbondioxide drying of methanol zinc borate mixtures”, *Ind. Eng. Chem. Res*., vol. 48, pp. 6869–6876, 2009.

[6] C. Ting, D. Jian-Cheng, W. Long-Shuo, and F. Gang, “Preparation and characterization of nano-zinc borate by a new method”, *J. Mater. Process. Tech*.,vol. 209, pp. 4076–4079, 2009.

[7] D. Gürhan, G. Ö. Çakal, İ. Eroğlu, and S. Özkar, Kesikli reaktörde çinko borat üretimini etkileyen parametrelerin incelenmesi, 1. National Boron Workshop Symposium Book, April 28-29, Ankara, 2005.

[8] D. Schubert, F. Alam, M. Visi, and C. Knobler, “Structural characterization and chemistry of the industrially important zinc borate $Zn[B_3O_4(OH)_3]$”, *Chem. Mater*.,v ol. 15, pp. 866-871, 2002.

[9] X. Shi, Y. Xiao, M. Li, L. Yuan, and J. Sun, “Synthesis of an industrially important zinc borate, $2ZnO{\cdot}3B_2O_3{\cdot}3H_2O$, by a rheological phase reaction method” *Powder Technol*., vol. 186,pp. 263-266, 2008.


**Nurcan Tugrul** was born in Gaziantep in 1973. Tugrul was graduated from B.Sc.,M.Sc. and Ph.D. in Chemical Eng. Department at YildizTechnicalUniversity, Istanbul. Her research interest is in the area of chemical technologies, evaluation of industrial wastes, food drying. She has many articles and studies in international and national conference proceedings and articles.

**Azmi Seyhun Kipcak** was graduated from Department of Chemical Engineering in EgeUniversity in 2002. After completing the university studies he graduated from Bilgi University from the department of Master of Business Administration in 2004. He worked in Kultur University from 2003 to 2007 as a research assistant then he transferred to YildizTechnical University at 2008, where he started his M.Sc. studies about Chemical Engineering in 2006. He completed his M.Sc. and Ph.D. studies at Yildiz Technical University in 2009 and 2013, respectively. He studied on neutron shielding with boron minerals and the characterization of boron minerals by using XRD, XRF, FT-IR, Raman, DTA/TG, DSC and ICP-OES at the M.Sc. studies and studied on the synthesis of magnesium borates from different raw materials and wastes at the Ph.D. Also he is improving the neutron shielding studies with the synthesized materials and working on the element analysis of Turkish Teas and Coffees. Another research field about the studies he is working is the zinc borate synthesis.

**Nil Baran Acarali** was graduated from B.Scin Food Eng. Department at Trakya Univ., Edirne in 2000, both M.Sc. and Ph.D. in Chemical Eng. Department at Yildiz Tech. Univ., Istanbul in 2003 and 2008, respectively. She has published nine articles in science citation index, over twenty nine studies in international conference proceedings and national proceedings. Her articles have fourty two cited references. The research interests are supercritical fluids technology, polymer technology, boron technology, fly ash characterization and heavy metal adsorption. The research field in boron technology is zinc borate production. Dr. BaranAcarali is an online member of boron research.

**Emek Moroydor Derun** was born in Istanbul in 1976. Moroydor Derun was graduated from B.Sc. in 1998, M.Sc. in 2000 and Ph. D. in 2005 from Chemical Engineering Department at Yildiz Technical University, Istanbul. Her research interest is in the area of waste management, lightweight concrete, semiconductive materials and boron technology. She has many articles and studies in international and national conference proceedings and articles.

**Sabriye Piskin** graduated from Istanbul Technical University on Chemical Engineering with M.Sc. degree in 1974. She completed a Ph.D. degree at the same department in 1983. Her research interests include boron minerals and compounds, hydrogen storage technologies, fuel cell applications, materials characterization, coal, waste management, corrosion, implants and synthetic materials production.