

Hydrated Magnesium Borate Synthesis from $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ at 80°C by Hydrothermal Method

A. S. Kipcak, P. Gurses, E. Moroydor Derun, and S. Piskin

Abstract—Borate minerals have attracted considerable attention in the past years due to their structural chemistry and mechanical properties in several industries. Recently, increasing attention has been paid to the use of; synthetically produced magnesium borates as catalysts reinforcing material for plastics, the conversion of hydrocarbons, electro-conductive treating agent, anti-wear and anti-corrosion materials. Magnesium borates can be synthesized by several methods such as; hydrothermal and solid-state (thermal) processes. In this study the hydrothermal production method was applied at the modest temperature of 80°C along with convenient crystal growth. Using $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, H_3BO_3 , and NaOH as starting materials, 30, 60, 120, 240 minutes of reaction times were studied. After all, 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 “Admontite” and “Mcallisterite” minerals were synthesized.

Keywords—FT-IR, hydrothermal method, magnesium borates, XRD.

I. INTRODUCTION

BORATE minerals have many potential application areas due to their structural chemistry and mechanical properties [1]. So far, many kinds of borate systems have been widely studied according to their special useful areas as well as to their form of presence such as; being in nature or synthesizing in the laboratory [2]. Magnesium borates have become an attractive support for the use of synthetically produced magnesium borates as catalysts reinforcing material for plastics [3], wide band gap [4], also anti-wear, and anti-corrosion materials [5].

The synthesis of magnesium borates occur using several methods such as hydrothermal and thermal processes [6]. Most of these methods for synthesizing magnesium borate need multistep, involving liquid or gas phase processes as well as long reaction periods and high energy needs [7]-[9].

A. S. Kipcak is with 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, seyhunkipcak@gmail.com).

P. Gurses is with Yildiz Technical University, Department of Chemical Engineering, Davutpasa Campus, 34210 Esenler, Istanbul, Turkey (e-mail: pelingurses@gmail.com).

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

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

Therefore, it is necessary to develop a simple, cost effective technique to prepare magnesium borate powders. Considering all above mentioned points and due to the effect in minimizing thermal strain in crystals, hydrothermal production method was applied with a modest temperature in order to secure better nucleation control [10], [11]. The basic principle of this process is to use heat energy to induce chemical reaction and change material structure as well as properties.

Before conducting the experiment, the studies in literature were investigated thoroughly. In the study of [12], $\text{MgBO}_2(\text{OH})$ nanowhiskers were produced with hydrothermal method by using $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, H_3BO_3 , and NaOH as raw materials at 200°C for 12h. Using the raw materials $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, H_3BO_3 , and NaOH , [13] produced $[\text{MgBO}_2(\text{OH})]$ with the reaction parameters 240°C and 18h. After the synthesis with hydrothermal method, magnesium borate hydroxide was calcined in order to obtain $\text{Mg}_2\text{B}_2\text{O}_5$ nanowhiskers. Keeping the molar ratio $\text{Mg}:\text{B}:\text{Na}$ as 2:3:4, $\text{MgBO}_2(\text{OH})$ was synthesized using MgCl_2 , H_3BO_3 and NaOH as starting materials in the study of Reference [14]. The isothermal condition was kept at 240°C for 18h.

The aim of this study is to synthesize hydrated magnesium borates using $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, H_3BO_3 , and NaOH with hydrothermal synthesis method used in the above-mentioned literature studies. Differently from the used reaction parameters in literature, shorter reaction times (30, 60, 120, and 240 minutes) and decreased reaction temperature (80°C) were applied in our experiments. XRD and FT-IR spectroscopy analysis were used to identify the synthesized magnesium borate powders.

II. EXPERIMENTAL

A. Raw Material Preparation and Characterization

Boric acid (H_3BO_3) was supplied from the Eti Bank Bandirma Boron and Acid Plant in Balikesir, Turkey. Then it was crushed, grinded with agate mortar (Fig. 1 (a)) and sieved (Fig. 1 (b)) to a particle size below 75 microns.

The other raw materials, magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) and sodium hydroxide (NaOH) were provided from Sigma-Aldrich and Merck Chemicals, respectively, both with 99.9% purity.

Boric acid powders were subjected to X-Ray Diffraction (XRD) analysis, Philips PANalytical brand (Fig. 2) with $\text{Cu-K}\alpha$ radiation at the parameters of 45kV and 40mA was used [15].



Fig. 1 (a) Grinding process, (b) Sieving process



Fig. 2 Philips PANalytical XRD

To identify and characterize the raw materials, "Vibration Spectroscopy" has been effectively used. Infrared spectra were recorded in the range $650\text{-}1800\text{cm}^{-1}$, with Perkin Elmer Spectrum One (Fig. 3) Fourier Transform Infrared Spectroscopy (FT-IR). In this analysis Universal ATR sampling accessory – Diamond/Zn was used and scan number was determined as 4 and resolution set as 4cm^{-1} .

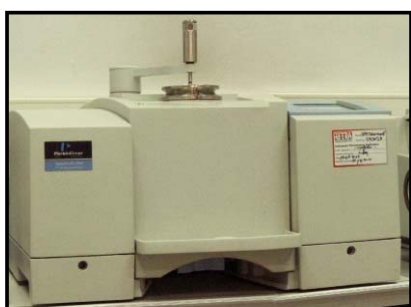


Fig. 3 Perkin Elmer Spectrum One FT-IR

B. Hydrothermal Synthesis of Magnesium Borates

Magnesium borate has been synthesized by two step process as synthesizing with the hydrothermal method and purification with alcohol after the reaction. In the synthesis the mole ratio of, which was determined with pre-experiments, 1:8:2 ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}:\text{H}_3\text{BO}_3:\text{NaOH}$) was used. The temperature of 80°C and reaction times of 30, 60, 120, 240 minutes was used in the experiments. The basic principle of this process is to use heat energy to induce chemical reaction and change

material structure as well as properties. After the reaction, the mixture was filtered through the filter paper and the mixture below the filter paper was dried in a dryer at 40°C . Finally, the solid was washed thoroughly with pure alcohol (96%), supplied from Merck Chemicals, in order to remove any excess boric acid content. The purified white precipitate was dried in EcoCell model oven again at 40°C , and finally collected for characterization analysis.

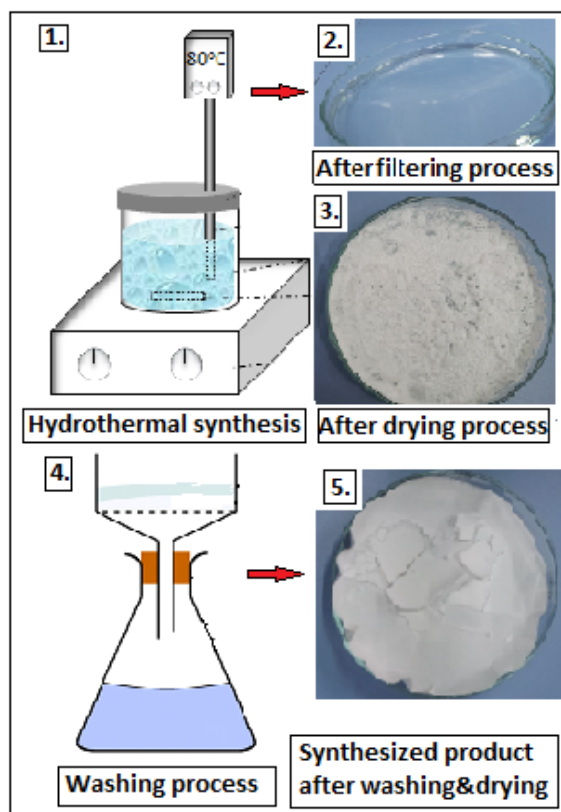


Fig. 4 Magnesium borate production steps

C. Characterization of Synthesized Magnesium Borates

The crystal structure and the morphology of the products were examined by X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FT-IR) with the parameter sets aforementioned before.

III. RESULTS AND DISCUSSION

A. Raw Material Characterization Results

XRD results and pattern of H_3BO_3 were shown in Table I and Fig. 5, respectively.

TABLE I
XRD RESULTS OF H_3BO_3

Raw Material	Reference Code	Mineral Name	Mineral Formula	Score
Boric acid	01-073-2158	Sassolite	H_3BO_3	62

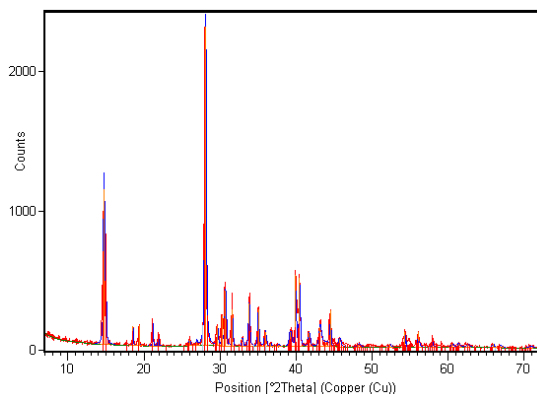


Fig. 5 XRD pattern of boric acid

The XRD pattern of boric acid shown in Fig. 4 was well matched to the standard diffraction pattern of Sassolite with powder diffraction file (pdf) number “01-073-2158”.

FT-IR spectrums of the boric acid, magnesium chloride hexahydrate and sodium hydroxide were shown in Fig. 6 and Table II, respectively.

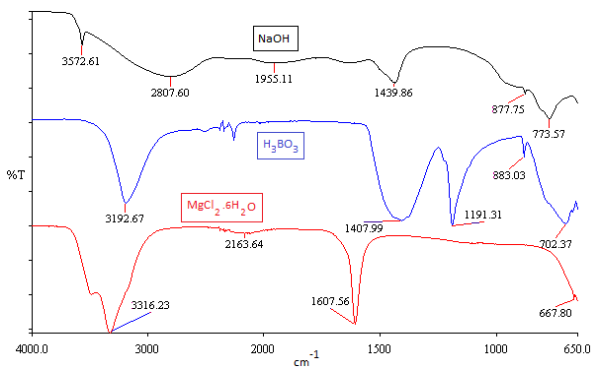


Fig. 6 FT-IR spectrums of the raw materials

The FT-IR spectra of NaOH exhibited the following absorptions and they were assigned referring to the literature [16]. The band at around 3600cm^{-1} is assigned as the characteristic peak of O-H tension from OH groups. From the FT-IR analysis, the spectrums were scanned with the FT-IR ATR inorganic library and the results are given in Table II.

According to the results boric acid and magnesium chloride hexahydrate were verified.

TABLE II
FT-IR ATR INORGANIC LIBRARY RESULTS

Score	Library Code	Mineral Name	Mineral Formula
0.704	AI0031	Boric acid	H_3BO_3
0.864	AI0084	Magnesium chloride hexahydrate	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$

B. Synthesized Magnesium Borate XRD Results

XRD patterns and results of the synthesized magnesium borates are shown in Fig. 7 and Table III, respectively.

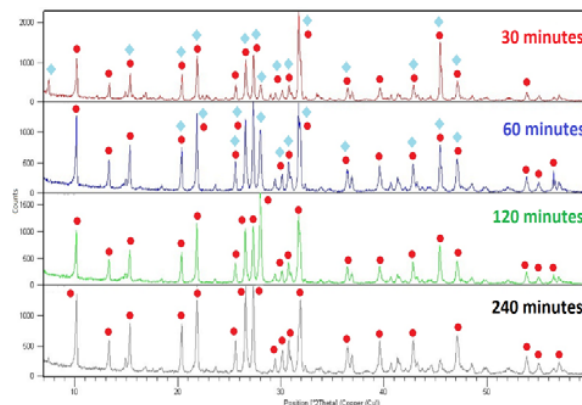


Fig. 7 XRD patterns of the synthesized magnesium borates;

● Mcallisterite, ◆ Admontite

TABLE III
XRD RESULTS OF THE SYNTHESIZED MAGNESIUM BORATES

Reac. Time	Pdf #	Mineral Name	Mineral Formula	Score
30	01-076-0540	Admontite	$\text{MgO}(\text{B}_6\text{O}_7)_3 \cdot 7\text{H}_2\text{O}$	40
	01-070-1902	Mcallisterite	$\text{Mg}_2(\text{B}_6\text{O}_7)(\text{OH})_6 \cdot 9\text{H}_2\text{O}$	83
60	01-076-0540	Admontite	$\text{MgO}(\text{B}_6\text{O}_7)_3 \cdot 7\text{H}_2\text{O}$	5
	01-070-1902	Mcallisterite	$\text{Mg}_2(\text{B}_6\text{O}_7)(\text{OH})_6 \cdot 9\text{H}_2\text{O}$	86
120	01-070-1902	Mcallisterite	$\text{Mg}_2(\text{B}_6\text{O}_7)(\text{OH})_6 \cdot 9\text{H}_2\text{O}$	83
240	01-070-1902	Mcallisterite	$\text{Mg}_2(\text{B}_6\text{O}_7)(\text{OH})_6 \cdot 9\text{H}_2\text{O}$	90

The XRD patterns of all the samples presented the similar profiles. “01-076-0540” and “01-070-1902” pdf numbered “Admontite” and “Mcallisterite” minerals were formed at two reaction times of 30 and 60 minutes. As the reaction time increased from 30 minutes to 60 minutes, the score of Mcallisterite minerals raised, whereas the score of Admontite minerals decreased noticeably. Because formed Admontite mineral structure was turned to Mcallisterite form.

As the reaction time increased from 60 minutes to 120 and 240 minutes, Admontite peaks were disappeared. It indicated that pure Mcallisterite minerals were obtained with the reaction times at 120 and 240 minutes. It can also be seen that the Mcallisterite score increases and peaks become sharper at 240 minutes, which is indicative of better crystallization that can be seen in the XRD crystal scores.

C. Synthesized Magnesium Borate FT-IR Results

FT-IR peak list and spectrums of the samples were shown in Table IV and Fig. 8, respectively.

TABLE IV
PEAK LIST OF FT-IR RESULTS

Product Code	30 min	60 min	120 min	240 min	Peak Interpretation
Peak 1	1411.64	1411.97	1410.92	1411.09	$\nu_{\text{as}}(\text{B}_{(3)}-\text{O})$
Peak 2	1337.36	1337.28	1336.97	1336.73	$\nu_{\text{as}}(\text{B}_{(3)}-\text{O})$
Peak 3	1240.39	1241.86	1240.44	1240.10	$\delta(\text{B}-\text{O}-\text{H})$
Peak 4	1055.88	1056.29	1054.96	1055.09	$\nu_{\text{as}}(\text{B}_{(4)}-\text{O})$
Peak 5	965.74	966.22	965.02	965.40	$\nu_{\text{s}}(\text{B}_{(3)}-\text{O})$
Peak 6	857.72	857.97	857.53	857.50	$\nu_{\text{as}}(\text{B}_{(4)}-\text{O})$
Peak 7	811.92	812.44	811.61	810.92	$\nu_{\text{s}}(\text{B}_{(4)}-\text{O})$
Peak 8	671.55	671.86	670.84	671.12	$\gamma(\text{B}_{(3)}-\text{O})$

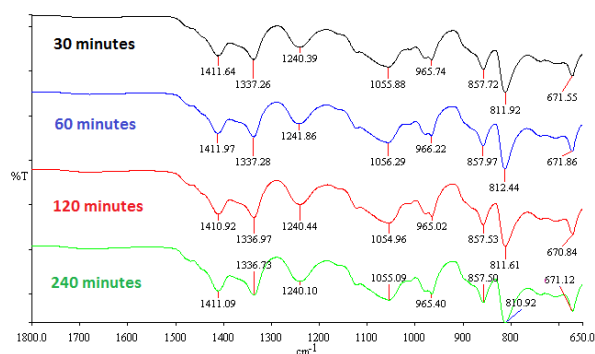


Fig. 8 FT-IR spectra of the synthesized minerals

As seen from the results, the FT-IR spectrums of the samples were assigned referring to literature [7], [8], [17]. According to Fig. 6, peak 1 between band values 1411.97 and 1410.92 cm^{-1} was due to the asymmetric stretching of $\text{B}_{(3)}\text{-O}$. Also, peak 2 was assigned to this formation. The band value between 1241.86 and 1240.10 cm^{-1} was in-plane bending of B-O-H. Peak 4 and peak 6 can be contributed to the $\text{B}_{(4)}\text{-O}$ asymmetric stretching vibrations in the value of 1056.29 - 1054.96 cm^{-1} and 857.97-857.50 cm^{-1} , respectively. In addition, the symmetric stretching vibration of the $\text{B}_{(3)}\text{-O}$ was observed between 966.22 and 965.02 cm^{-1} , for peak 5. Peak 7 band values change between 812.44 and 810.92 cm^{-1} , indicated the symmetric stretching of $\text{B}_{(4)}\text{-O}$. Lastly, peak 8 can be attributed to the bending of three coordinate boron with bands between 671.86 and 670.84 cm^{-1} .

IV. CONCLUSIONS

With the conducted experiments, it was aimed to research the influence of the reaction time on the synthesized product. With this target, certain reaction parameters, such as mole ratio of raw materials, reaction temperature and drying temperature were selected and determined with pre-experiments. As seen from the outcomes of XRD analysis, increasing reaction time from 30 minutes to 240 minutes proved that the score of Mcallisterite minerals rose gradually. Increasing time to 120 and 240 minutes, the structure of Admontite minerals turned to Mcallisterite structure, which indicated pure Mcallisterite minerals were formed. However, at the reaction time of 240 minutes, sharper peaks and better crystal structure were monitored comparing to other reaction times.

From all the results, it is nearly the same in all the recorded FT-IR spectra of magnesium borates. In addition, the results of FT-IR analysis represented nearly the same band values of characteristic peaks of Magnesium Boron Hydrates. Comparing to the other literature studies, our results with more pure magnesium borate powders demonstrate that this hydrothermal production method we use is not only a simple and cost-effective way but also a technique which is helpful in the synthesis of other magnesium borates.

REFERENCES

- [1] P. Zhao, L. Cheng, G. Yang, "Synthesis and characterization of a new organic-inorganic hybrid zinc borate: $[\text{Zn}(\text{dab})_{0.5}(\text{dab}')_{0.5}(\text{B}_4\text{O}_6(\text{OH})_2)] \cdot \text{H}_2\text{O}$ ", *Inorganic Chemistry Communications*, vol. 20, pp. 138-141, 2012
- [2] A.F. Qasrawi, T. S. Kayed, A. Mergen, M. Gürü "Synthesis and characterization of $\text{Mg}_2\text{B}_2\text{O}_5$ ", *Materials Research Bulletin*, vol. 40, pp. 583-589, 2005.
- [3] S. Li, X. Fang, J. Leng, H. Shen, Y. Fan, D. Xu, "A new route for the synthesis of $\text{Mg}_2\text{B}_2\text{O}_5$ nanorods by mechano-chemical and sintering process", *Material Letters*, vol. 64, pp. 151-153, 2010.
- [4] A.S. Kipcak, F. T. Senberber, E. Moroydor Derun, S. Piskin, "Hydrothermal Synthesis of Magnesium Borate Hydrates from MgO and H_3BO_3 at 80°C", *Research Bulletin of the Australian Institute of High Energetic Materials*, vol. 1, pp. 47-55, 2011.
- [5] U. Dosler, M. M. Krzmcanc, D. Suvorov, "The synthesis and microwave dielectric properties of $\text{Mg}_3\text{B}_2\text{O}_6$ and $\text{Mg}_2\text{B}_2\text{O}_5$ ceramics", *Journal of the European Ceramic Society*, vol. 30, pp. 413-418, 2010.
- [6] E. Moroydor Derun, A. S. Kipcak, E. Gurel, S. Piskin, "Microwave Assited Solid-State Synthesis of Magnesium Borate Hydrates at 270 W", *ICCE 2012: International Conference on Chemical Engineering*, 28-29 November 2012, Paris, 2012.
- [7] L. Zhihong, H. Mancheng, "New synthetic method and thermochemistry of szaibelyite", *Thermochimica Acta*, vol. 411, pp. 27-29, 2004.
- [8] L. Zhihong, H. Mancheng, "Synthesis and thermochemistry of $\text{MgO} \cdot 3\text{B}_2\text{O}_3 \cdot 3.5\text{H}_2\text{O}$ ", *Thermochimica Acta*, vol. 403, pp. 181-184, 2003.
- [9] L. Kumari, W. Z. Li, S. Kulkarni, K.H. Wu, W. Chen, C. Wang, "Effect of Surfactants on the Structure and Morphology of Magnesium Borate Hydroxide Nanowhiskers Synthesized by Hydrothermal Route", *Nanoscale Res Lett*, vol. 5, pp. 149-157, 2010.
- [10] C. D. McMillen, H. G. Giesber, J. W. Kolis, "The hydrothermal synthesis, growth, and optical properties of $\gamma\text{-LiBO}_2$ ", *Journal of Crystal Growth*, vol. 310, pp. 299-305, 2008.
- [11] W. Zhu, L. Xiang, Q. Zhang, X. Zhang, L. Hu, S. Zhu, "Morphology preservation and crystallinity improvement in the thermal conversion of the hydrothermal synthesized $\text{MgBO}_2(\text{OH})$ nanowhiskers to $\text{Mg}_2\text{B}_2\text{O}_5$ nanowhiskers", *Journal of Crystal Growth*, vol. 310, pp. 4262-4267, 2008.
- [12] W. Zhu, G. Li, Q. Zhang, L. Xiang, S. Zhu, "Hydrothermal mass production of $\text{MgBO}_2(\text{OH})$ nanowhiskers and subsequent thermal conversion to $\text{Mg}_2\text{B}_2\text{O}_5$ nanorods for biaxially oriented polypropylene resins reinforcement", *Powder Technology*, vol. 203, pp. 265 - 271, 2010.
- [13] W. Zhu, Q. Zhang, L. Xiang, F. Wei, X. Sun, X. Piao, S. Zhu, "Flux-Assisted Thermal Conversion Route to Pore-Free High Crystallinity Magnesium Borate Nanowhiskers at a Relatively Low Temperature", vol. 8, pp. 2938-2945, 2008.
- [14] W. Zhu, X. Zhang, L. Xiang, S. Zhu, "Hydrothermal Formation of the Head-to-Head Coalesced Szaibelyite $\text{MgBO}_2(\text{OH})$ nanowires", *Nanoscale Research Letters*, vol. 4, pp.724-731, 2009.
- [15] A. S. Kipcak, F. T. Senberber, E. Moroydor Derun, S. Piskin, "Evaluation of the Magnesium Wastes with Boron Oxide in Magnesium Borate Synthesis", *ICEBESE 2012: International Conference on Environmental, Biological, and Ecological Sciences, and Engineering*, 25-26 July, Amsterdam - The Netherlands, Vol. 67, pp. 678-683, 2012.
- [16] M.A. Lillo-Rodenas, D. Cazorla-Amoros, A. Linares-Solano, "Understanding chemical reactions between carbons and NaOH and KOH An insight into the chemical activation mechanism", *Carbon*, vol. 41, pp.267-275, 2003.
- [17] J. Yongzhong, G. Shiyang, X. Shuping, L. Jun, "FT-IR spectroscopy of supersaturated aqueous solutions of magnesium borate", *Spectrochimica Acta Part A*, vol. 56, pp. 1291-1297, 2000.



Pelin Gurses was born in Istanbul in 1988. Gurses graduated B.Sc. in Chemical Eng. Department at Yildiz Technical University, Istanbul, in 2011. She is currently continuing M.Sc. education at the same university. Gurses is interested in synthesis and characterization of magnesium borate minerals and derivatives. She is working as a Product Development Engineer at Mercedes Benz Türk Bus Plant, as well.



Azmi Seyhun Kipcak was graduated from Department of Chemical Engineering in Ege University 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 Yildiz Technical 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.



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, semi conductive 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.