

Evaluation of the Magnesium Wastes with Boron Oxide in Magnesium Borate Synthesis

A. S. Kipcak, F. T. Senberber, E. Moroydor Derun, S. Piskin

Abstract—Magnesium wastes and scraps, one of the metal wastes, are produced by many industrial activities, all over the world. Their growing size is becoming a future problem for the world. In this study, the use of magnesium wastes as a raw material in the production of the magnesium borate hydrates are aimed. The method used in the experiments is hydrothermal synthesis. The conditions are set to, waste magnesium to B_2O_3 , 1:3 as a molar ratio. Four different reaction times are studied which are 30, 60, 120 and 240 minutes. For the identification analyses X-Ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FT-IR) and Raman spectroscopy techniques are used. As a result at all the reaction times magnesium borate hydrates are synthesized and the most crystalline forms are obtained at a reaction time of 120 minutes. The overall yields of the production are found between the values of 65-80 %.

Keywords—Hydrothermal synthesis, magnesium borates, magnesium wastes, boron oxide

I. INTRODUCTION

THE increase in the rate of waste formation will be a problem for future of the world due to storage and disposal of wastes. In recent years, studies about waste storage and evaluation are done to solve this problem. Some kinds of waste are hazardous for people and environment. One of the dangerous wastes is metal wastes and scraps. Distribution of waste per person in the United States and Turkey are 8.9% and 7% of metal waste, respectively [1].

Evaluation of wastes is getting more interesting for industrial activities more than storage because of the increasing cost of raw materials and energy. One of the evaluation method is recycle process. Steps of metal waste recycling process are a separate collection, magnetic extraction, smelting factory, recycled metal, comprises the steps of the new metal products. Metal wastes are 1% of solid wastes and 3% of the recovered waste [2]. Magnesium wastes and scraps are produced by many industrial activities, all over the world. Magnesium is a chemical element with the symbol Mg, atomic number 12, and common oxidation number +2.

Elemental magnesium is a fairly strong, silvery-white, light-weight metal (two thirds the density of aluminum). It tarnishes slightly when exposed to air.

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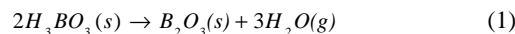
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It is an alkaline earth metal and the eighth most abundant element in the Earth's crust and ninth in the known universe as a whole. Magnesium is the fourth most common element in the Earth as a whole (behind iron, oxygen and silicon), making up 13% of the planet's mass and a large fraction of planet's mantle [3]-[5].

Boron is the chemical element with atomic number 5 and the chemical symbol B. The atomic mass is 10.81. It is a low-abundance element in both the solar system and the Earth's crust. However, boron is concentrated on Earth by the water-solubility of its more common naturally occurring compounds, the borate minerals such as boric acid and borax. Turkey has 72.2% of the boron minerals that are present in the world, which can sufficiently meet world's needs for many years. Approximately world's total reserves are reported to be 1.2 billion tons [6], [7].

Boric acid, also called hydrogen borate having chemical formula H_3BO_3 , is a weak acid of boron often used as an antiseptic, insecticide, flame retardant, as a neutron absorber, and as a precursor of other chemical compounds. It exists in the form of colorless crystals or a white powder and dissolves in water. Sometimes written $B(OH)_3$. When occurring as a mineral, it is called sassolite [8]. Boron oxide can easily be formed from the following reaction:



Magnesium borate production is useful because of minerals superior properties of thermal and mechanic characters. Main properties of magnesium borate minerals are high heat resistance, corrosion resistance and high coefficient of elasticity. So this boron group can be used in ceramic industry, in the production of superconducting materials, in the composition of detergents, due to the content of boron in the friction-reducing additives in oils and insulating coating compositions [9].

Magnesium borates can be synthesized by liquid-state or solid-state methods. In literature, synthesized magnesium borate minerals with liquid-state method can be listed $MgBO_2(OH)$ [10], $MgO \cdot 3B_2O_3 \cdot 17H_2O$ [11], $MgO \cdot 3B_2O_3 \cdot 3,5H_2O$ [12], $2MgO \cdot 2B_2O_3 \cdot MgCl_2 \cdot 14H_2O$ [13], $2MgO \cdot B_2O_3 \cdot H_2O$ and $MgO \cdot 3B_2O_3 \cdot 7H_2O$ [14]. Synthesized magnesium borate minerals with solid-state method can be listed $Mg_2B_2O_5$ [15]-[17], $Mg_3B_2O_6$ [18], [19]. The common feature of all studies done as a raw material MgO or MgOH is to use in synthesis.

In this study, magnesium wastes are used as magnesium source in magnesium borate production. It can be called as a new perspective in evaluation of metal wastes.

II. EXPERIMENTAL

A. Raw Material Preparation and Characterization

Magnesium wastes (Fig. 1 (a)) are retrieved from local gold factory in Turkey where these wastes are formed at the instance of plastic molding in the manufacturing processes. These wastes are to be stored in the factory.

Boron oxide is retrieved from the Boron Management Plant in Eskisehir, Turkey. These boron oxides are grinded with agate mortar (Fig. 1 (b)) and sieved (Fig. 1 (c)) to a particle size below 75 microns.

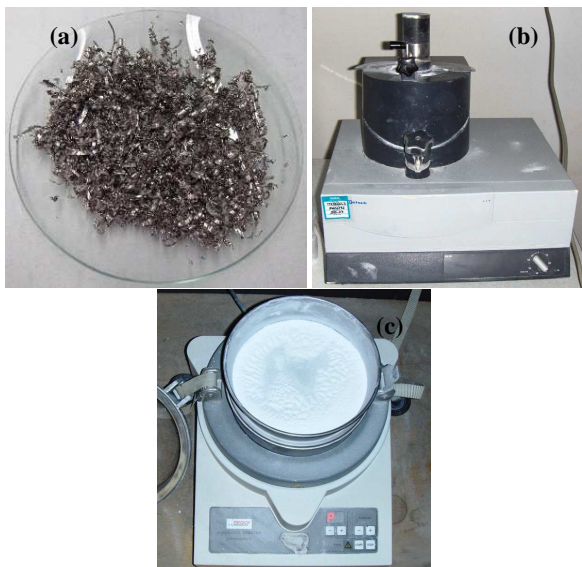


Fig. 1 (a) Waste Mg, (b) Grinding process, (c) Sieving process

Magnesium wastes and boron oxide are subjected to X-Ray Diffraction (XRD) analysis with Philips PANanalytical brand (Fig. 2 (a)) where in this equipment X-rays are produced from Cu-K α tube at the parameters of 45kV and 40mA [6].

Magnesium wastes are subjected to X-Ray Fluorescence (Fig. 2 (b)) analysis by Philips PANanalytical brand Minipal Model 4 with silicon drift detector [20].



Fig. 2 (a) Philips PANanalytical XRD, (b) Philips PANanalytical XRF

Also magnesium wastes are analyzed with Scanning electron microscope with Energy Disperse Spectroscopy (SEM-EDS) by CamScan Apollo 300 field-emission SEM (Fig. 3) and EDS detector brand is Oxford.

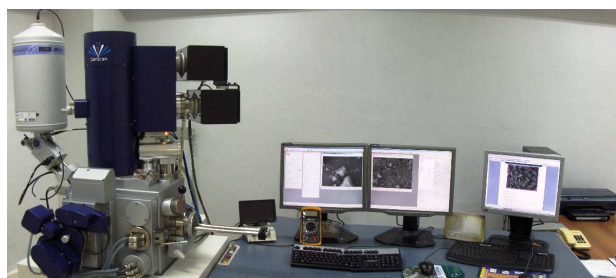


Fig. 3 CamScan Apollo 300 SEM

Boron oxide is subjected to Perkin Elmer Spectrum One (Fig. 4 (a)) Fourier Transform Infrared Spectroscopy (FT-IR) and Perkin Elmer Brand, Raman Station 400F Raman Spectroscopy (Fig. 4 (b)) techniques. In the FT-IR technique Universal ATR sampling accessory – Diamond / ZnSe is used and measurement range is selected as 4000–650 cm^{-1} , scan number is 4 and resolution set as 4 cm^{-1} . For Raman Spectroscopy, the parameters of exposure time (seconds) and number of exposures was set to 4. Measurement range is selected as 3280–250 cm^{-1} and data interval was selected as 2 cm^{-1} [20].

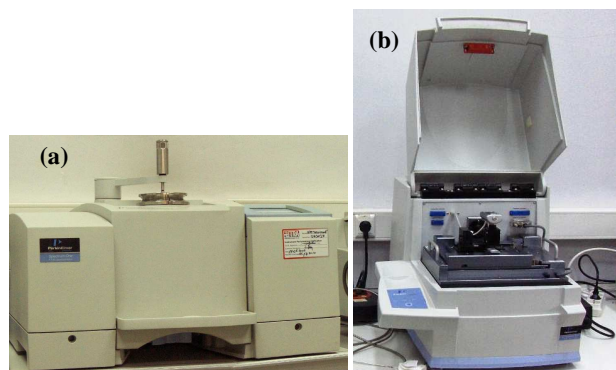
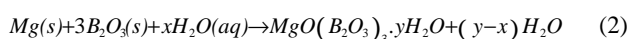


Fig. 4 (a) Perkin Elmer Spectrum One FT-IR, (b) Raman Station 400F Raman Spectroscopy

B. Hydrothermal Synthesis of Magnesium Borates

For the hydrothermal synthesis, starting molar ratio of waste magnesium to boron oxide is selected as 1:3. The liquid phase is used as ultra-pure water (18.3 $\text{m}\Omega\cdot\text{cm}$) that is produced from the equipment of Human Power I+ Water Purification System.

Experiment temperature is selected as 80°C, and four different reaction times are conducted to investigate the phase transition between different types of magnesium borates according to the reaction time changes. The reaction times are set to 30, 60, 120 and 240 minutes. The formation reaction of magnesium borates are shown in (2).



After the reaction, the first filtration process is used for the removal of excess magnesium and other trace amount of metals inside the waste magnesium. In this process, 80°C hot water is used for the washing and dispersing the synthesized magnesium borates below the filter paper. After that the slurry content is dried in EcoCell model oven at 40°C. The dried content was washed and filtered with pure alcohol (96°), supplied from Merck Chemicals, in order to remove excess boric acid content that is formed in the hydrothermal reaction as a byproduct. The byproduct reaction is shown in (3). Then the filtered content was dried in EcoCell model oven again at 40°C.



C. Characterization of the Synthesized Magnesium Borates

At this step synthesized materials are subjected to XRD, FT-IR and Raman techniques with the parameter set explained at part II.A. "Raw Material Preparation and Characterization".

III. RESULTS AND DISCUSSION

A. Raw Material Characterization Results

XRD patterns of the waste magnesium and boron oxide are shown in Fig. 5 and Fig.6 respectively.

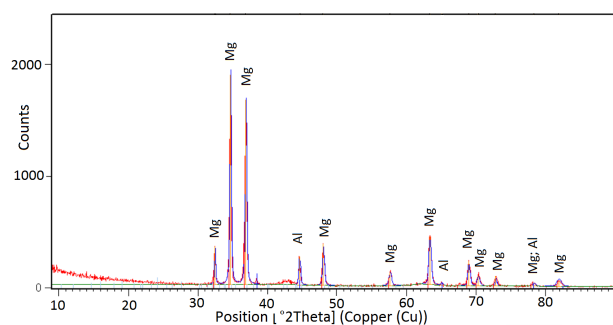


Fig. 5 XRD pattern of waste magnesium [21]

From the waste magnesium XRD pattern, the major peaks represents the 01-089-5003 numbered powder diffraction file (pdf) magnesium also some aluminum minor peaks are observed with pdf number of 01-089-2769 [21].

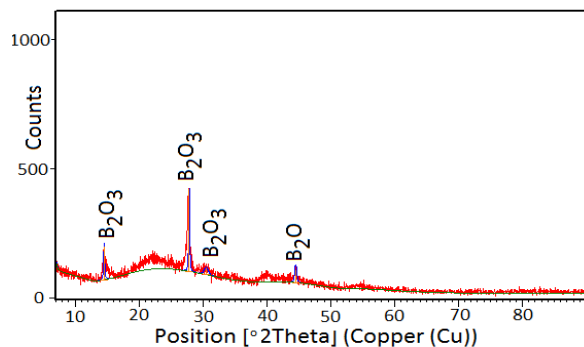


Fig. 6 XRD pattern of boron oxide

From the boron oxide XRD pattern, two different types of "boron oxide" minerals are found. Major peaks represent the "B₂O₃" formulated and pdf numbered "00-006-0297" boron oxide and minor peak represents the "B₂O" formulated and pdf numbered "01-088-2485" boron oxide.

XRF and SEM-EDS results of the waste magnesium is shown in Table I.

TABLE I
XRF AND SEM-EDS RESULTS OF THE WASTE MAGNESIUM [21]

Elements	XRF	SEM-EDS
	Content (%)	Content (%)
Mg	93.30	93.12
Al	3.67	3.54
Zn	0.88	1.72
Mn	0.90	1.02
S	0.08	0.21
Ca	0.11	0.14
Cr	0.03	-
Fe	0.93	-
Cu	0.14	0.25

Both XRF and SEM-EDS results showed that the element in the waste magnesium is "magnesium" and the minor element is "aluminum". Other elements can be classified as trace elements. XRF and SEM-EDS analysis supports the XRD analysis.

FT-IR and Raman spectrums of the boron oxide are shown in Fig. 7 and Fig. 8 respectively.

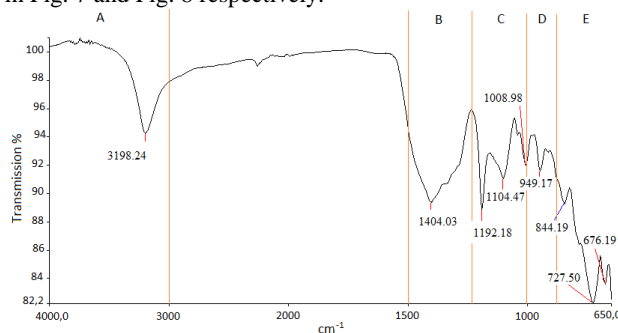


Fig. 7 FT-IR spectrum of the boron oxide

According to the FT-IR analysis of the boron oxide, peak intervals can be classified in five groups. Part A can be explained with the OH⁻ groups of the mineral that can be attached to mineral from the humidity of the air. Part B shows the asymmetric stretching of tri-coordinate boron (B₍₃₎-O). In part C, the peak peaks between 1192.18 and 1008.98 mean asymmetric stretching of four-coordinate boron (B₍₄₎-O). Symmetric stretching of B₍₃₎-O can be seen in Part D and at the end of the spectrum, Part E explains the out-of-plane OH⁻ bending band and bending of B₍₃₎-O in the structure.

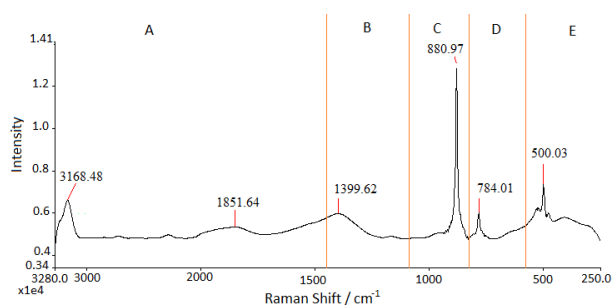


Fig. 8 Raman spectrum of the boron oxide

According to Raman spectrums of B_2O_3 , the first and second peaks in part A might be the OH groups in the minerals that can be attached to mineral from the humidity of the air. The peaks of asymmetric stretching of $B_{(4)}-O$ is seen in part B. In part C, the peak can be explain with the symmetric stretching of $B_{(3)}-O$. In part D symmetric stretching of $B_{(4)}-O$ is seen. Peak on part E, might be explain with the bending of $B_{(3)}-O$.

B. Synthesized Magnesium Borate XRD Results

XRD patterns and results of the synthesized magnesium borates are shown in Fig. 9 and Table II respectively.

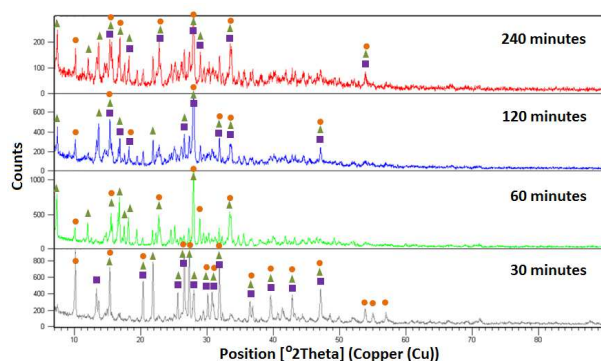


Fig. 9 XRD patterns of the synthesized magnesium borates;
 ● Mcallisterite, ▲ Admontite, ■ Magnesium borate hydrate

TABLE II
 XRD RESULTS OF THE SYNTHESIZED MAGNESIUM BORATES

Reac. Time	Pdf #	Mineral Name	Mineral Formula	Score
30	01-076-0540	Admontite	$MgO(B_2O_3)_3 \cdot 7H_2O$	26
	01-070-1902	Mcallisterite	$Mg_2((B_6O_7)(OH)_6)_2 \cdot 9H_2O$	82
	01-073-0638	MgBH*	$MgB_6O_7(OH)_6 \cdot 3(H_2O)$	26
60	01-076-0540	Admontite	$MgO(B_2O_3)_3 \cdot 7H_2O$	73
	01-070-1902	Mcallisterite	$Mg_2((B_6O_7)(OH)_6)_2 \cdot 9H_2O$	38
	01-076-0540	Admontite	$MgO(B_2O_3)_3 \cdot 7H_2O$	48
120	01-070-1902	Mcallisterite	$Mg_2((B_6O_7)(OH)_6)_2 \cdot 9H_2O$	50
	01-073-0638	MgBH*	$MgB_6O_7(OH)_6 \cdot 3(H_2O)$	19
	01-076-0540	Admontite	$MgO(B_2O_3)_3 \cdot 7H_2O$	45
240	01-070-1902	Mcallisterite	$Mg_2((B_6O_7)(OH)_6)_2 \cdot 9H_2O$	35
	01-073-0638	MgBH*	$MgB_6O_7(OH)_6 \cdot 3(H_2O)$	13

* MgBH: Magnesium Borate Hydrate

From the XRD results obtained it is seen that “01-076-0540” and “01-070-1902” pdf numbered “Admontite” and “Mcallisterite” minerals are formed at all reaction times. 30

minutes after the reaction mcallisterite type of magnesium borate mineral is formed majorly and admontite and MgBH minerals formed also. At the reaction time of 60 minutes all MgBH and partly mcallisterite minerals are changed to admontite minerals. 120 minutes after the reaction some of the admontite minerals are changed to mcallisterite and MgBH minerals oppositely at a reaction time of 60 minutes. After the 240 minutes all minerals scores are decreased, means that their crystalline structures became less crystal than at the reaction time of 120 minutes.

C. Synthesized Magnesium Borate FT-IR Results

FT-IR spectrums of synthesized minerals are shown in Fig 10.

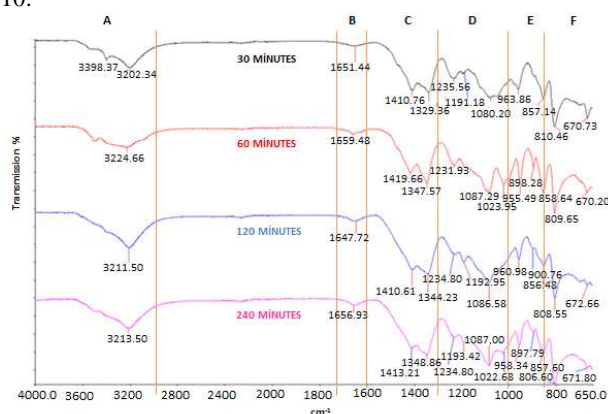


Fig. 10 FT-IR spectrum of synthesized minerals

In the FT-IR spectrums the peak values between 3398.37 and 3202.34 cm^{-1} that are also seen in the B_2O_3 raw material and these peaks are might be the OH- group. At the peaks around 1650 cm^{-1} is different peak group from B_2O_3 , can be explained with the water groups in the minerals. The peaks with 1419.66 and 1329.36 cm^{-1} might be the asymmetric stretching of tri-coordinate boron ($B_{(3)}-O$). The peaks between 1235.5618 and 1022.68 cm^{-1} , might be the asymmetric stretching of tri-coordinate boron ($B_{(4)}-O$). Symmetric stretching of $B_{(3)}-O$ can be seen between 693.86 and 857.14 cm^{-1} . Other peaks between 810.46 and 670.20 cm^{-1} explains the out-of-plane OH¹ bending band and bending of $B_{(3)}-O$ in the structure.

D. Synthesized Magnesium Borate RAMAN Results

Raman spectrums of synthesized minerals are shown in Fig. 11. According to Raman spectrums of products, the first peaks in part A also seen on B_2O_3 Raman spectrum that might be the OH groups in the minerals. The peaks of asymmetric stretching of $B_{(4)}-O$ is seen in part B. In part C, the peak values between 961.98 and 880.68 cm^{-1} can be explain symmetric stretching of $B_{(3)}-O$. The characteristic band of Magnesium boron hydrates is seen at the bands between 640.17 and 635.88 cm^{-1} , namely $V_p[B_6O_7(OH)_6]^{2-} / V_p[[B_3O_3(OH)_4]^-]$, in part D. Peaks of part E, might be explain with the bending of $B_{(3)}-O$. Part F includes the peaks of bending of $B_{(4)}-O$.

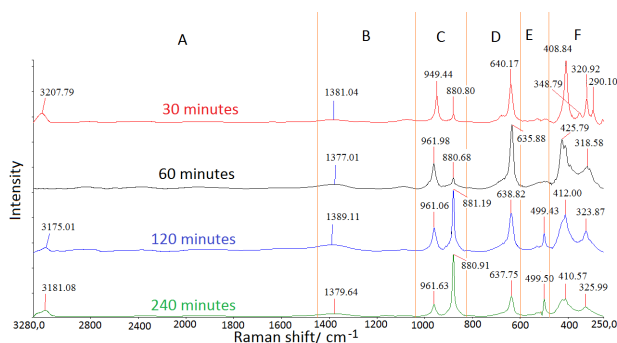


Fig. 11 Raman spectrums of the synthesized magnesium borates

IV. CONCLUSIONS

Evaluation of wastes is getting more difficult day after day since the increase of the industrial activities. Also the storage of these wastes are bigger problem than the evaluation. The use of wastes as a raw material are became interesting because of the decreasing cost of raw materials and energy. Therefore in this study magnesium wastes are used as a raw material in the production of magnesium borate production. From the results of this study it is seen that magnesium wastes can be used in the hydrothermal synthesis of magnesium borates at such a low temperatures of 80°C. From the experiment results obtained in the laboratory the overall yields of the production are found between the values of 65-80 %.

REFERENCES

- [1] T. R. Ministry of Education, "Environmental protection, solid waste collection", Ankara, 2009.
- [2] T. R. Ministry of Environment and Forestry, General Directorate of Environmental Management, "Waste management action plan (2008-2012)", Ankara, 2008.
- [3] P. F. Bernath, J. H. Black, J. W. Brault, "The spectrum of magnesium hydride", *Astrophysical Journal*, vol. 298, pp. 375-381, 1985.
- [4] L. B. Railsback, *Some Fundamentals of Mineralogy and Geochemistry*. (Retrieved 09.02.2012).
- [5] C. E. Housecroft, A. G. Sharpe, *Inorganic Chemistry*, Prentice Hall, 2008, pp. 305-30.
- [6] A. S. Kipcak, The investigation of the usability of boron minerals as a neutron shielding material. Yildiz Technical University, M.Sc. Thesis, Istanbul, 2009 [in Turkish].
- [7] E. Moroydor Derun, A. S. Kipcak, "Characterization of some boron minerals against neutron shielding and 12 year performance of neutron permeability", *J Radioanal Nucl Chem*, to be published.
- [8] A. S. Kipcak, F. T. Senberber, E. Moroydor Derun, S. Piskin, "Solid State Synthesis of Magnesium Borates at 800°C from Periclase and Sassolite", *3rd Conference on Chemical Engineering and Advanced Materials (CEAM 2011-VF)*, Naples - Italy, Nov 2011.
- [9] A. S. Kipcak, F. T. Senberber, E. Moroydor Derun, S. Piskin, "Hydrothermal synthesis of magnesium borate hydrates from MgO and H₃BO₃ at 80°C", in *2011 Research Bulletin of the Australian Institute of High Energetic Materials*, Australia, vol. 1, pp. 47-55 (2011).
- [10] W. Zhu, G. Li, Q. Zhang, L. Xiang, S. Zhu, "Hydrothermal mass production of MgBO₂(OH) nanowhiskers and subsequent thermal conversion to Mg₂B₂O₅ nanorods for biaxially oriented polypropylene resins reinforcement", *Powder Technology*, vol. 203, pp. 265 - 271, 2010.
- [11] L. Zhiyong, H. Mancheng, G. Shiyang, "Studies on synthesis, characterization and thermochemistry of Mg₂[B₂O₄(OH)₂]·H₂O", *Journal of Thermal Analysis and Calorimetry*, vol. 75, pp. 73 - 78, 2004.
- [12] L. Zhihong, H. Mancheng, "Synthesis and thermochemistry of MgO·3B₂O₃·3.5H₂O", *Thermochim Acta.*, vol. 403, pp. 181 - 184, 2003.
- [13] L. Zhihong, H. Mancheng, "New synthetic method and thermochemistry of szaibelyite", *Thermochim Acta*, vol. 411, 27 - 29, 2004.
- [14] L. Dou, J. Zhong, H. Wang, "Preparation and characterization of magnesium borate for special glass" *Physica Scripta*, vol. 30, pp. 413-418, 2010.
- [15] S. Li, X. Fang, J. Leng, H. Shen, Y. Fan, D. Xu, "A new route for the synthesis of Mg₂B₂O₅ nanorods by mechano - chemical and sintering process", *Mater. Lett.*, vol. 64, pp. 151 - 153, 2010.
- [16] E. M. Elssfah, A. Elsanousi, J. Zhang, H. S. Song, C. Tang, "Synthesis of magnesium borate nanorods", *Materials Letters*, vol. 61, pp. 4358 - 4361, 2007.
- [17] Y. Zeng, H. Yang, W. Fu, L. Qiao, L. Chang, J. Chen, H. Zhu, M. Li, G. Zou, "Synthesis of magnesium borate (M₂B₂O₅) nanowires, growth mechanism and their lubricating properties" *Materials Research Bulletin*, vol. 43, pp. 2239 - 2247 2008.
- [18] U. Dosler, M. M. Krzmacz, D. J. Suvorov, "The synthesis and microwave dielectric properties of Mg₃B₂O₆ and Mg₂B₂O₅ ceramics", *Eur Ceram Soc.*, vol. 30, pp. 413- 418, 2010.
- [19] H. Guler, F. Kurtulus, E. Ay, G. Celik, I. Dogan, "Solid-State and Microwave-Assisted synthesis and characterization of Mg₂B₂O₅ ve Mg₃(BO₃)₂", IV International Boron Symposium, October, 2009.
- [20] A. S. Kipcak, F. T. Senberber, E. Moroydor Derun, S. Piskin, "Characterization of Magnesium Borate Hydrates Produced from MgO and H₃BO₃ at 80°C, for two Different Drying Temperatures", *12th Mediterranean Congress of Chemical Engineering*, November, 2011.
- [21] A. Kanturk, Borate compounds of different compositional, Metal Borohydride as Hydrogen Storage Media Production and Analysis of the Mechanism of Production. Yildiz Technical University, PhD Thesis, Istanbul, 2011 [in Turkish].



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Tugce Senberber was graduated from B.Sc. in 2010. She is studying at her M.Sc. thesis. She is interested in synthesis and characterization of boron minerals and waste management.



Emek Moroydor Derun was born in Istanbul in 1976. Moroydor Derun 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. She has more than fifty articles and eighty conference manuscripts pressed at the international area.