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The Effect of Waste Magnesium to Boric Acid Ratio in Hydrothermal Magnesium Borate Synthesis at 70^{o}C

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Abstract**—**Magnesium wastes are produced by many industrial activities. This waste problem is becoming a future problem for the world. Magnesium borates have many advantages such as; high corrosion resistance, heat resistance, high coefficient of elasticity and can also be used in the production of material against radiation. Addition, magnesium borates have great potential in sectors including ceramic and detergents industry and superconducting materials.

In this study, using the starting materials of waste magnesium and H_3BO_3 the hydrothermal method was applied at a moderate temperature of 70^{o}C. Several mole ratios of waste magnesium to H_3BO_3 are selected as; 1:2, 1:4, 1:6, 1:8, 1:10. Reaction time was determined as 1 hour. After the synthesis, X-Ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FT-IR) techniques are applied to products. As a result the forms of mcallisterite "$Mg_2(B_6O_7(OH)_6)_2.9(H_2O)$", admontite "$MgO(B_2O_3)_3.7(H_2O)$" and magnesium boron hydrate ($MgO(B_2O_3)_3.6(H_2O)$" are obtained.

Keywords**—**Hydrothermal synthesis, magnesium borates, waste magnesium.

I. Introduction

RESPONDING to unlimited human needs on higher levels with the help of technology makes it inevitable for the environment and human health to be faced with serious threats as the natural resources are increasingly destroyed and each product manufactured is finally transformed into waste[1]. 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 [2].

Both in the production and marketing phases, through minimizing the production of waste materials, the excessive pressure on the natural resources should be prevented; of course in the consumption phase, the production of wastes should be minimized and the remaining waste materials should be recycled and transformed from waste to an input to the economy [1].

Magnesium is a chemical element with the symbol Mg, atomic number 12, and common oxidation number +2. Magnesium is the lightest of all design metals. It's light in weight just like a plastic material and also tough like a metal. It's high specific toughness and rigidity, good machinability, castability and weldability with known methods makes it attractive for chemical industry. Also magnesium's scrap material can be used in recycling processes all over the world [3].

Boron, the fifth element in the periodic table, has widespread commercial uses.Boron (B) has an atomic weight of 10.81 g/molwith two isotopes, ^{10}B and ^{11}B, neither of which is radioactive [4], [5].Because boron is electron-deficient, it has a strong affinity for electron donors such as oxygen, which explains the absence of boron in its elemental form in nature. Boron containing minerals are almost all inorganic salts of boron and commercially important deposits are found in the United States, Turkey, South America, Russia, and China [6]. In addition, boron as borates or boric acid is ubiquitously present in soil, water, and food where its presence is due to its being an essential element for plant growth [4], [5].

In the United States today, the major uses of boron minerals and chemicals include manufacture of glass, especially glass fibers, ceramics, detergents and bleaches, alloys and metals, fire retardants, fertilizers and increasingly wood preservatives. The European Borates Association listed EU uses as includingglass (insulationfiberglass, textilefiberglass, borosilicateglass), ceramics, detergents (perborates), cleaning materials, cosmetics, flame retardants, fertilizers, wood preservatives, industrial fluids (metal-working, antifreeze, brake fluids, motor oil), metallurgy, and miscellaneous chemical formulations. The Chinese MiningAssociation reported that borax and boric acid are used in the chemical industry, the light industry, in medicines, building materials, and other uses [6].

Boric acid can be produced from the reactions of various boron minerals (such as colemanite, ulexite and borax) with various acid solutions (such as hydrochloric acid, phosphoric acid, sulfuric acid, propionic acid, acetic acid, and nitric acid) and these reactions were widely investigated in earlier studies which were mostly focused on determining reaction kinetics and the effects of reaction temperature, stirring rate, particle size of the colemanite ore, and acid concentration on the reaction rate [7]. Commercially, the most used boron compound is boric acid. In Turkey, boric acid is produced through the reaction between colemanite and sulphuric acid [8].

Boric acid is an inexpensive, nontoxic compound, and it is generally considered a green material.It is an excellent

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precursor for the preparation of various types of organoboranes and is also used as a mild Lewis acid catalyst for several organic transformations. α-Hydroxyamides are important synthetic intermediates in organic synthesis and also serve as valuable agents in medicinal chemistry [9].

Metal borates are remarkable ceramic materials with excellent mechanical properties and high resistance to corrosion and they possess attractive thermal properties [10]. There are many kinds of metal borates found not only in nature but also synthesized in the laboratory [11]. Some of these metal borates have different application areas due to their useful properties [12]. Magnesium borate which can besynthesized in the laboratory has been shown to be a thermoluminescence phosphor, a good antiwear, high heat resistance, corrosion resistance, supermechanical strength, superinsulation, light weight, high coefficient of elasticity and a reducing friction additive. $Mg_2B_2O_5$ is also a ferroelastic material. Thus, one-dimensional metal borate nanostructures can have potential applications in the fields of nanocomposites, nanomechanics, and nanoelectronics[9], [10].

Magnesium borates like the other metal borates are not only found in nature but also produced synthetically in the laboratory. Five hydrated magnesium borates belong to $MgO.3B_2O_3.nH_2O$ (n = 7.5, 7, 6, 5 and 3.5) are found up to now. It is also known that magnesium borates exist as compounds such as $3MgO.B_2O_3$ ($Mg_3B_2O_6$), $2MgO.B_2O_3$ ($Mg_2B_2O_5$), and $MgO.B_2O_3$ (MgB_2O_4). These magnesium borates have many potential application areas such as catalysts useful for the conversion of hydrocarbons and as luminescent materials for use in fluorescent discharge lamps, cathode ray tube screens, and X-ray screens. It may be also used as fused cast refractory that possesses corrosion–erosion resistance in basic oxygen steel making environments and high degree of thermal shock resistance. Finally, it is used as electroconductive treating agent or as a reinforcing material for plastics [12].

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 as; $MgBO_2(OH)$ [13], $MgO.3B_2O_3.17H_2O$ [14], $MgO.3B_2O_3.3,5H_2O$ [15], $2MgO.2B_2O_3.MgCl_2.14H_2O$ [16], $2MgO{\cdot}B_2O_3{\cdot}H_2O$ and $MgO{\cdot}3B_2O_3{\cdot}7H_2O$ [17]. Synthesized magnesium borate minerals with solid-state method can be listed $Mg_2B_2O_5$[18]-[20], $Mg_3B_2O_6$[21], [22]. The common feature of all studies done as a raw material MgO or $Mg(OH)_2$is to use in synthesis.

In this study, magnesium borate was synthesized by hydrothermal technique and magnesium wastes were used as magnesium source. It can be sample as a new perspective in evaluation of metal wastes.

II. Materials and Methods

A. Raw Material Preparation and Characterization

Magnesium wastes (Fig. 1 (a)) weretakenfrom local gold factory in Turkey.These wastes wereoccurred from the instance of plastic molding in the manufacturing processes where these wastes stored in the factory.

Boric acid (Fig. 1 (b)) was retrieved from the Boron Management Plant in Bandırma, Turkey. It was grinded with agate mortar (Fig. 1 (c)) and sieved (Fig. 1 (d)) to a particle size below 74 microns.

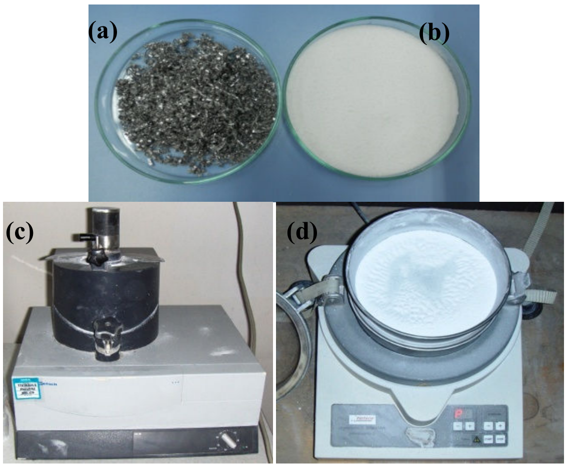

Fig.1 (a) Waste Mg, (b) Boric acid (c) Grinding process (d) Sieving process

Magnesium wastes and boric acid were subjected to X-Ray Diffraction (XRD) analysis with Philips PANalytical brand (Fig. 2 (a)) where in this equipment X-rays were produced from Cu-Kα tube at the parameters of 45kV and 40mA [4].

Magnesium wastes were subjected to X-Ray Fluorescence (Fig. 2 (b)) analysis by Philips PANalytical brand Minipal Model 4 with silicon drift detector [23].

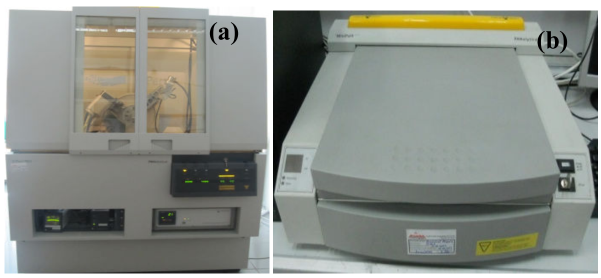

Fig. 2 (a) Philips PANalytical XRD (b) Philips PANalytical XRF

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

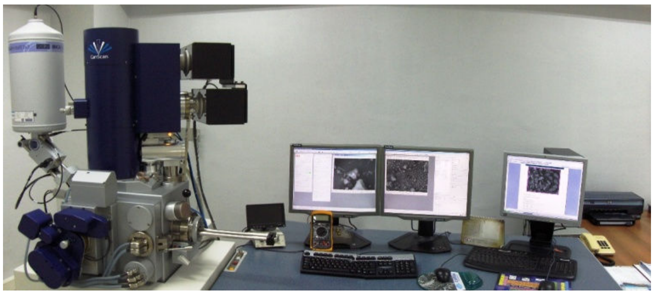

Fig. 3 CamScan Apollo 300 SEM

Boric acid was subjected to Perkin Elmer Spectrum One (Fig. 4)Fourier Transform Infrared Spectroscopy (FT-IR) and Perkin Elmer Brand, techniques. In the FT-IR technique Universal ATR sampling accessory – Diamond / ZnSe is used and measurement range is selected as 4000–650cm^{-1}, scan number is 4 and resolution set as 4cm^{-1}.

Fig. 4 Perkin Elmer Spectrum One FT-IR

B. Hydrothermal Synthesis of Magnesium Borates

For the hydrothermal synthesis, starting molar ratio of waste magnesium to boric acid was selected as 1:2, 1:4, 1:6, 1:8, 1:10. The liquid phase wasused as ultra-pure water (18.3 mΩ.cm) that was produced from the equipment of Human Power I+ Water Purification System.

Experiment temperature was selected as 70^{o}C, and four different reaction concentrations (1:2, 1:4, 1:6, 1:8, 1:10) were conducted to investigate the phase transition between different types of magnesium borates according to the reaction concentration changes.

After the reaction, the first filtration processwas used for the removal of excess magnesium and other trace amount of metals inside the waste magnesium. In this process, 70^{o}C water was used for the washing and dispersing the synthesized magnesium borates below the filter paper. After that the slurry content was dried in Ecocell model oven at 40^{o}C. The dried content was washed and filtered with pure alcohol (96^{o}), supplied from Merck Chemicals, in order to remove excess boric acid content that wasunreacted in the hydrothermal reaction.Then the filtered content was dried in Ecocell model oven again at 40^{o}C.

C.Characterization of the Synthesized Magnesium Borates

At this step synthesized materials were subjected to XRD and FT-IR techniques with the parameter set explained at part II.A.

III.Results and Discussion

A. Raw Material Characterization Results

XRD patterns of the waste magnesium and boric acid were shown in Figs. 5 and 6 respectively.

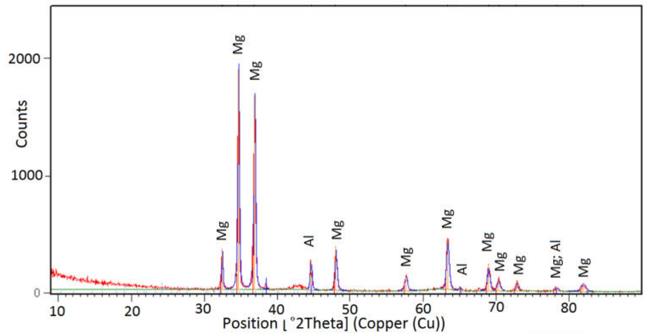

Fig. 5 XRD pattern of waste magnesium [24].

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 [24].

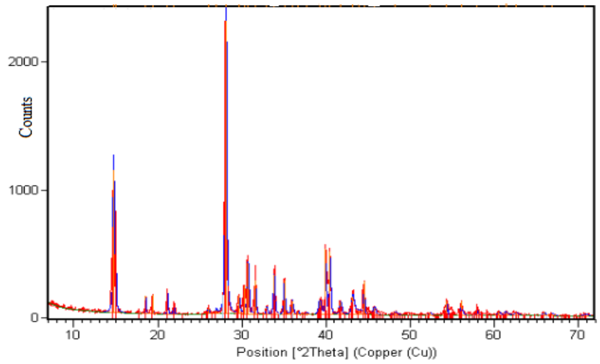

Fig. 6 XRD pattern of boric acid

From the boric acid XRD pattern, peaks represents the “H_3BO_3 (Sassolite)” formulated and pfd numbered “01-073-2158’’boric acid.

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

TABLE I
XRF and SEM-EDS Results of the Waste Magnesium[24]

Elements	XRF Content (%)	SEM-EDS 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 major 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 spectrum of the boric acid is shown in Fig. 7.

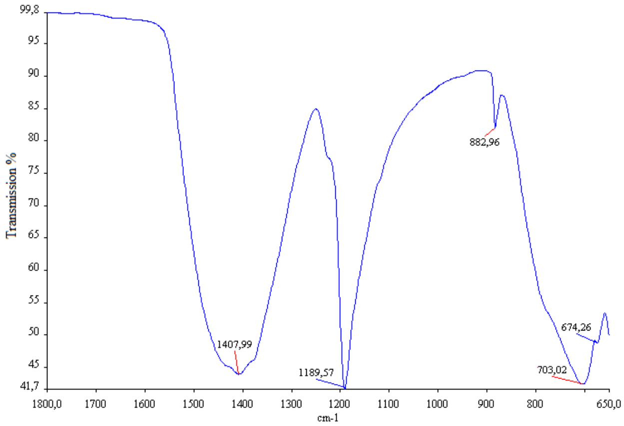

Fig. 7 FT-IR spectrum of the boric acid

According to the FT-IR analysisof the boric acid, the first peak at 1407.99 cm^{-1} shows the asymmetric stretching of tri-coordinate boron ($B_{(3)}$–O). The peaks at 1189.57 cm^{-1} represents four coordinate boron asymmetrical stretching. Symmetric stretching of $B_{(3)}$–O can be seen at 882.96 cm^{-1}. The last peaks with 703.02 and 674.26 cm^{-1} explains the out-of-plane OH^{-1} bending band and stretching of $B_{(3)}$–O in the structure.

B. Synthesized Magnesium Borate XRD Results

XRD patterns and results of the synthesized magnesium borates were shown in Fig. 8 and Table II respectively.

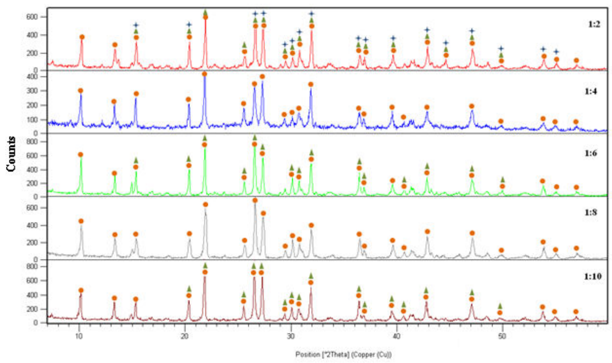

Fig. 8 XRD patterns of the synthesized magnesium borates; ●Mcallisterite, ▲Admontite

TABLE II
XRD RESULTS OF THE SYNTHESIZED MAGNESIUM BORATES

Reac. Time	Mineral Code	Mineral Formula	Score
1:2	Admontite	$MgO(B_2O_3)_3.7H_2O$	28
	Mcallisterite	$Mg_2((B_6O_7)(OH)_6)_2.9H_2O$	82
	MgBH*	$MgO(B_2O_3)_3.3(H_2O)_6$	26
1:4	Mcallisterite	$Mg_2((B_6O_7)(OH)_6)_2.9H_2O$	76
1:6	Admontite	$MgO(B_2O_3)_3.7H_2O$	20
	Mcallisterite	$Mg_2((B_6O_7)(OH)_6)_2.9H_2O$	85
1:8	Mcallisterite	$Mg_2((B_6O_7)(OH)_6)_2.9H_2O$	83
1:10	Admontite	$MgO(B_2O_3)_3.7H_2O$	12
	Mcallisterite	$Mg_2((B_6O_7)(OH)_6)_2.9H_2O$	79

*Magnesium Boron Hydrate

From the XRD results obtained it is seen that "01-076-0540", "01-070-1902" and '' 01-076-0539'' pdf numbered "Admontite", "Mcallisterite" and ''Magnesium Boron Hydrate''minerals werefound at all the reaction concentrations. From the waste magnesium XRD pattern, the major peaks represent mcallisterite minerals and the minor peaks represent admontite and magnesium borate hydrate minerals. The highest mcallisterite and admontite formations were seen on 1:2 and 1:6; pure mcallisterite formation was obtained in 1:4 and 1:8 rates of reaction concentration. Magnesium boron hydrate formation was only seen on 1:2 rate of reaction concentration.

C. Synthesized Magnesium Borate FT-IR Results

FT-IR spectrums of synthesized minerals were shown in Fig 9.

TABLE III
XRD POWDER DIFERACTION FILES OF MINERALS

Pdf #	**Mineral Code**
01-076-0540	Admontite
01-070-1902	Mcallisterite
01-076-0539	MgBH

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

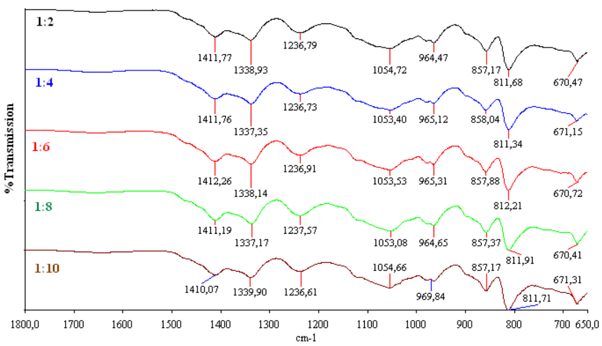

Fig. 9 FT-IR spectrums of synthesized minerals

In the FT-IR spectrums the peak values between 1412.26 and 1410.07cm^{-1}represents the three coordinate boron asymmetrical stretching. Other two peaks at around 1339.90and 1236.61cm^{-1} was OH^{-1} in plane stretching due to the crystal waters inside the magnesium borates.The peaks with 1054.72 and 954.65cm^{-1}represents four coordinate boron asymmetrical stretching.Symmetric stretching of $B_{(3)}$–O can be seen between 858.04and 857.08cm^{-1}.Also in magnesium borates OH^{-1} out of plane stretching was seen between 812.21and 811.34cm^{-1}. The last peak represents the stretching of three coordinate boron with the peaks values at around 670 cm^{-1}.

IV. Conclusions

Amount of the waste products are increasing all over the world. Also the storage of this waste is the other serious problem. The use of waste, as a raw material providesenergy efficiency and decreases the cost of raw materials. Therefore in this study magnesium wastes were used as a raw material in 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 moderate temperature of 70^{o}C. The analysis results (XRD and FT-IR) showed that combined hydrothermal synthesis of magnesium borates in different concentrations. From the experiment results obtained the overall yields of the productions were found between 45-75 %.

References

[1] O., Kose, S., Ayaz., B., Koroglu, ‘’Waste Management in Turkey - National Regulations and Evaluation of Implementation Results’’ Performance Audit Report, 2007.
[2] T. R. Ministry of Education, “Environmental protection, solid waste collection”, Ankara, 2009.
[3] O. Atalay, Magnezyum ve alasımlarının konstrüksiyon malzemesi olarak otomotivde kullanımı. Istanbul Technical University, M.Sc. Thesis, Istanbul, 2006 [in Turkish].
[4] 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].
[5] E. MoroydorDerun, A. S. Kipcak, “Characterization of some boron minerals against neutron shielding and 12 year performance of neutron permeability”, JRadioanalNuclChem, to be published.
[6] A. R. Scialli, J. P. Bonde, I. Hohlfeld, B. D. Culver,Y. Li, F. M. Sullivan,’’ An overview of male reproductive studies of boron with an emphasis on studies of highly exposed Chinese workers‘’, Reproductive Toxicology, vol. 29, pp. 10-24, 2010.
[7] B. Kuskay, A.N. Bulutcu, ‘’Design parameters of boric acid production process from colemanite ore in the presence of propionic acid’’, Chemical Engineering and Processing, vol.50, pp. 377–383, 2011.
[8] Z. Ekıncı, E. Sayan, A.V. Bese, O. N. Ata, ‘’Optimization and modeling of boric acid extraction from colemanite in water saturated with carbon dioxide and sulphur dioxide gases’’ Internatıonal Journal of Mıneral Processıng, vol. 82, pp. 187–194, 2007.
[9] J. S. Kumar, Subash C. Jonnalagadda, V. R. Mereddy, ‘’An efficient boric acid-mediated preparation of a-hydroxyamides’’, Tetrahedron Letters, vol. 51, pp. 779–782, 2010.
[10] Y. Li, Z. Fan, J. G. Lu, R. P. H. Chang, ‘’Synthesis of Magnesium Borate ($Mg_2B_2O_5$) Nanowires by Chemical Vapor Deposition Method’’, Chemistry of Materials, vol.16, pp. 2512-2514, 2004.
[11] L. Jun, G. Shiyang, X. Shuping, L. Bing, H. Rongzu, ‘’Thermochemistry of hydrated magnesium borates’’, The Journal of Chemical Thermodynamics, vol. 29, pp. 491-497, 1997.
[12] A.F. Qasrawi, T.S. Kayed, A. Mergen, M. Guru, ‘’Synthesis and characterization of $Mg_2B_2O_5$’’, Materials Research Bulletin, vol. 40, pp. 583–589, 2005.
[13] W.Zhu, G.Li, Q.Zhang, L.Xiang, S.Zhu, “Hydrothermal mass production of $MgBO_2(OH)$ nanowhiskers and subsequent thermal conversion to $Mg_2B_2O_5$nanorods for biaxially oriented polypropylene resins reinforcement”, Powder Technology, vol. 203, pp. 265 – 271, 2010.
[14] L. Zhiyong, H. Mancheng, G. Shiyang, “Studies on synthesis, characterization and thermochemistry of $Mg_2[B_2O_4(OH)_2]$ H_2O”, Journal of Thermal Analysis and Calorimetry, vol. 75, pp. 73 – 78, 2004.
[15] L. Zhihong, H. Mancheng, “Synthesis and thermochmistry of $MgO.3B_2O_3.3,5H_2O$”, *ThermochimActa*., vol. 403, pp. 181 – 184, 2003.
[16] L. Zhihong, H. Mancheng, “New synthetic method and thermochemistry of szaibelyite”, *ThermochimActa,* vol. 411, 27 – 29, 2004.
[17] L.Dou, J.Zhong, H.Wang, “Preparation and characterization of magnesium borate for special glass”*PhysicaScripta*,vol. 30, pp. 413– 418, 2010.
[18] S. Li, X. Fang, J. Leng, H. Shen, Y. Fan, 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.
[19] 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.
[20] Y.Zeng, H.Yang, W.Fu, L.Qiao, L. Chang, J. Chen, H.Zhu, M.Li, G. Zou, “Synthesis of magnesium borate ($M_2B_2O_5$) nanowires, growth mechanism and their lubricating properties” Materials Research Bulletin, vol. 43, pp. 2239 – 22472008.
[21] U. Dosler, M. M. Krzmanc, D. J. Suvorov, “The synthesis and microwave dielectric properties of $Mg_3B_2O_6$ and $Mg_2B_2O_5$ ceramics”, *Eur Ceram Soc,*vol.30, pp. 413– 418, 2010.
[22] H. Guler, F. Kurtulus, E. Ay, G. Celik, I. Dogan, *“Solid-State and Microwave-Assisted synthesis and characterization of $Mg_2B_2O_5$ve$Mg_3(BO_3)_2$*”, IV International Boron Symposium, October, 2009.
[23] A. S. Kipcak, F. T. Senberber, E. Moroydor Derun, S. Piskin, “Characterization of Magnesium Borate Hydrates Produced from MgO and H_3BO_3 at 80^{o}C, for two Different Drying Temperatures”, *12th Mediterranean Congress of Chemical Engineering*, November, 2011.
[24] A. S. Kipcak, Synthetic production of magnesium borates from different magnesium and boron sources by various methods and the investigation of their production parameters. Yildiz Technical University, Ph. D. Thesis, Istanbul, 2013 [in Turkish].

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