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Synthesis of Magnesium Borates from the Slurries of Magnesium Wastes by Microwave Energy

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***Abstract*—**In this research, it is aimed not only microwave synthesis of magnesium borates but also evaluation of magnesium wastes. Synthesis process can be described with the reaction of Mg wastes and boric acid using microwave energy. X-Ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FT-IR) were applied to synthesized minerals. According to XRD results, magnesium borate hydrate mixtures were obtained as mcallisterite (pdf# = 01-070-1902, $Mg_2(B_6O_7(OH)_6)_2.9(H_2O)$) at higher crystallinity properties was achieved at the mole ratio raw material 1:1. Also, other kinds of magnesium borate hydrates were obtained at lower crystallinity such as admontite (pdf # = 01-076-0540, $MgO(B_2O_3)_3.7(H_2O)$), inderite (pdf # = 01-072-2308, $2MgO.3B_2O_3.15(H_2O)$) and magnesium borate hydrates (pdf # = 01-076-0539, $MgO(B_2O_3)_3.6(H_2O)$). FT-IR spectrums indicated that minor changes were seen at the band values of characteristic stretching in each experiment. At the end of experiments it is seen that using microwave energy may contribute positive effects to design of synthesis process such as reducing reaction time and products at higher crystallinity.

***Keywords*—**Magnesium wastes, boric acid, magnesium borate, microwave energy.

I. Introduction

MICROWAVE energy means the non-ionizing electromagnetic radiation with frequencies in the range of 300 MHz to 300 GHz and has many applications in industry such as communication, cooking food, tempering and thawing, and curing of wood and rubber products [1]-[4]. There are several reports in the literature of non-thermal 'microwave effects' that accelerate reaction rates, alter reaction pathways and result in unique properties in polymers, ceramics and composites [2]. The microwave-assisted thermal and hydrothermal processes are often found to be rapid, and have the potential to enhance the crystallization kinetics of synthesis process [5]. Using microwave energy has superior advantages such as; reduced processing costs, better production quality, new materials and products, improved human health, reduced hazards to humans and the environment and enhanced quality of life and cleaner, and more economical than the conventional methods [1]-[4].

A variety of materials such as borates, carbides, nitrides, complex oxides, silicides, zeolites, apatite, etc. have been synthesized using microwaves [5]-[9]. Newalkar et al., investigated the microwave assisted-hydrothermal synthesis of barium titanate ($BaTiO_3$) [6]. Querol et al., synthesized zeolitic material from fly ash by conventional and microwave-assisted hydrothermal alkaline activation experiments [7]. Vicente et al., prepared the hectorite mineral ($M_x[Li_xMg_{6-x}Si_8O_{20}(OH)_4]$ (M=Na, Li, NH_4)) using the starting materials of SiO_2, $Mg(OH)_2$ and LiF by microwave assisted-autoclave [8]. Boxall and Lukehart (2001), studied the synthesis of Pt or Pd/Carbon nanocomposites using microwave irradiation [9].

One of the dangerous wastes is metal wastes and scraps. Metals, discharged or transported into the environment, may undergo transformations and can have adverse effects to the environment, public health and economy. Distribution of waste per person in the United States and Turkey are 8.9% and 7% of metal waste, respectively. Recent studies focus on the thermal and hydrothermal technologies for waste disposal. Magnesium wastes and scraps are produced by many industrial activities, all over the world. Waste of magnesium tarnishes slightly when exposed to air [10], [11].

Magnesium borates are the sub-group of boron minerals that have importance in industry due the properties of high heat resistance, corrosion resistance and high elasticity coefficient [12]. In magnesium borate synthesis, it generally requires higher reaction temperatures and longer reaction times [13]-[22].

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 these studies, it is seen that magnesium borate synthesis requires high reaction temperatures and long reaction times. In other words, synthesis procedure requires high energy.

In literature, there is not any special research for the microwave assisted synthesis of boron minerals. In this

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research, it is aimed both microwave synthesis of magnesium borates and evaluation of a type metal wastes as a raw material.

II. Experimental Procedure

A. Raw Material Preparation

Magnesium (Mg) wastes and boric acid (H_3BO_3) are used as starting materials in study. These wastes are formed at the instance of plastic molding in the manufacturing processes. They are stored in the factory. Mg wastes and H_3BO_3 are obtained from local gold factory in Turkey and the Boron Management Plant in Eskisehir-Turkey, respectively. Wastes are used without pre-treatment and H_3BO_3 mineral is grinded with RETSCH agate mortar and sieved (Figs. 1 (a) and (b)).

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

B. Synthesis Procedure

Synthesis procedure involves the stages of reaction with the help of microwave energy, separation of impurities and excess materials with filtration operation and drying.

Waste of magnesium and boric acid were mixed at different mole ratios varying between 1:1 and 1:8, then pure water added to mixture (approximately 80% H_3BO_3 w/w). The slurry mixture was put into microwave oven at 360 watts at reaction time of 2 minutes. After the reaction step, products were washed with ethyl alcohol (99.9%) and distilled water to separate the excess boric acid content and impurities of magnesium wastes, respectively.

C. Characterization Step

Obtained products are identified by using a Philips Panalytical X'Pert-Pro diffractometer with CuKα radiation at operating parameters of 40 mA and 45 kV with step size 0.02° and speed of 1°/min (Fig. 2).

Perkin Elmer Spectrum One (Fig. 3) is used for the Fourier Transform Infrared Spectroscopy (FT-IR). In the (FT-IR) technique Universal ATR sampling accessory– Diamond/ZnSe is used and measurement range is selected as 1800–650 cm^{-1}, scan number is 4 and resolution set as 4 cm^{-1} [12].

Magnesium wastes are subjected to X-Ray Fluorescence (Fig. 4) analysis by Philips PANanalytical brand Minipal Model 4 with silicon drift detector [12].

Fig. 2 Philips PANanalytical XRD

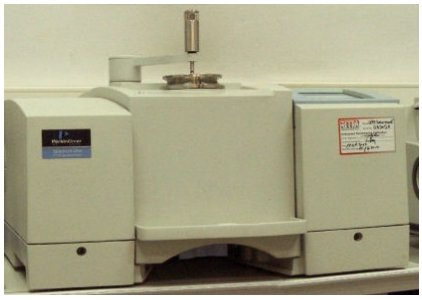

Fig. 3 Perkin Elmer Spectrum One FT-IR

Fig. 4 Philips PANanalytical XRF

III. Result and Discussion

A. Characterization Results of Raw Materials

Characterization results of magnesium wastes are given Fig. 5 and Table I. According to Fig. 5, metal wastes involve Mg as major component and Al and other impurities as minor component.

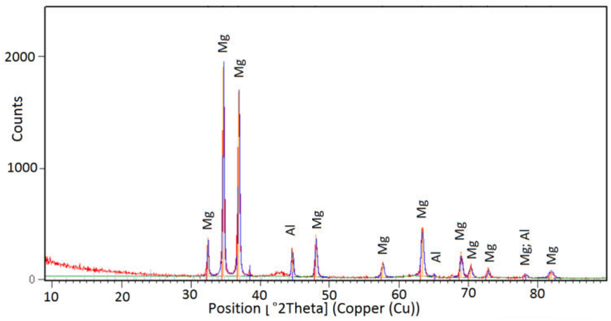

Fig. 5 XRD pattern of magnesium wastes [12]

In Table I, it is seen that these minor impurities inside wastes, which are very low percentage, can be described as Al, Zn, Mn, S, Ca, Cr, Fe and Cu.

TABLE I
XRF AND SEM-EDS RESULTS OF THE WASTE MAGNESIUM [12]

Elements	XRF Content (%)
Mg	93.30
Al	3.67
Zn	0.88
Mn	0.90
S	0.08
Ca	0.11
Cr	0.03
Fe	0.93
Cu	0.14

Characterization results of H_3BO_3 are given in Fig. 6 and 7. In Fig. 6, the highest intensity percentages (I%) of boric acid are seen at the 2θ values of 28.028°, 14.630° and 14.978°. According to XRD pattern of boric acid, boric acid mineral is identified as Sassolite with the powder diffraction file of “01-073-2158” and XRD score of 62.

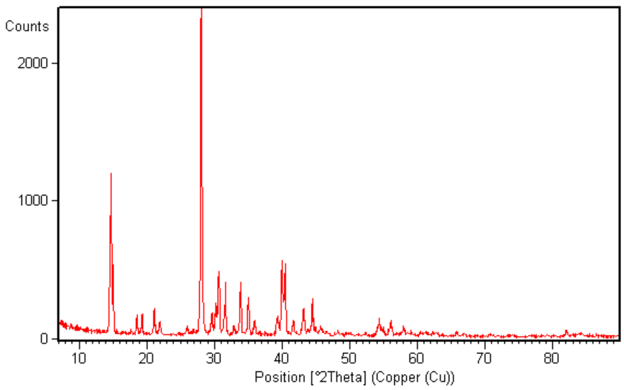

Fig. 6 XRD pattern of boric acid

In the FT-IR spectrum of boric acid (Fig. 7), characteristic vibrations are seen between the B and O atoms at the band values of 3195, 2515, 2362, 2261, 14737, 1193, 894, 704 cm^{-1}.

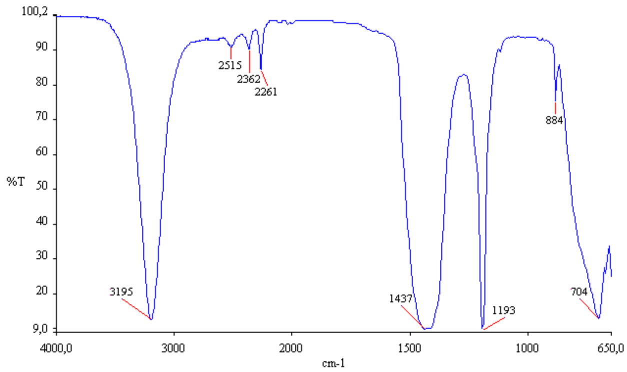

Fig. 7 FT-IR spectrum of boric acid

B. Characterization Results of Synthesized Materials

Characterization results of synthesized minerals are presented in Fig. 8, Table II and Fig. 9.

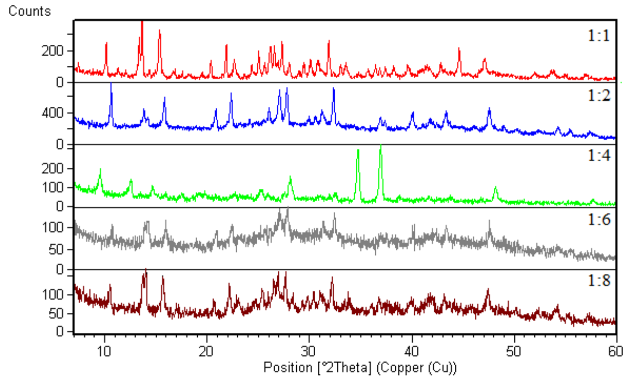

Fig. 8 XRD pattern of synthesized minerals

In the XRD pattern of synthesized minerals, it is seen that count values of peaks change with the changing of mole ratio of raw materials. The proper pattern due to proper crystal formation is seen at the mole ratio of 1:1 (Fig. 8).

TABLE II
XRD RESULTS OF SYNTHESIZED MINERALS

Mole Ratio	Obtained Phase Scores				
	P 1	P 2	P 3	P 4	P 5
1:1	70	22	-	21	-
1:2	36	-	-	-	12
1:4	22	-	6	-	-
1:6	12	-	-	-	-
1.8	32	-	7	-	-

P 1: 01-070-1902 Mcallisterite $[Mg_2(B_6O_7(OH)_6)_2.9(H_2O)]$
P 2: 01-076-0540 Admontite $[MgO(B_2O_3)_3.7(H_2O)]$
P 3: 01-072-2308 Inderite $[Mg(B_3O_3(OH)_5).5H_2O]$
P 4: 01-076-0539 Magnesium borate hydrate $[MgO(B_2O_3)_3.6(H_2O)]$
P 5: 01-073-1254 Aksaite $[Mg(B_6O_7(OH)_6).2H_2O]$

In all experiments major phase is identified as Mcallisterite mineral with the powder diffraction file number of “01-070-1902”and chemical formula of “$Mg_2(B_6O_7(OH)_6)_2.9(H_2O)$”, which is shown as *Phase 1* (P 1) in Table II. XRD scores of synthesized Mcallisterite increase with the increasing ratio of magnesium wastes in mixture. Hence, the highest XRD score is seen at the mole ratio of 1:1.

The minor phase formation, which is seen at lower crystallinity features in all experiments, changes by the chainging of mole ratio. These phases (P 2, 3, 4 and 5) are determined as P 2, 01-076-0540 Admontite [$MgO(B_2O_3)_3.7(H_2O)$]; P 3, 01-072-2308 Inderite [$Mg(B_3O_3(OH)_5).5H_2O$]; P 4, 01-076-0539 Magnesium borate hydrate [$MgO(B_2O_3)_3.6(H_2O)$] and P 5: 01-073-1254 Aksaite [$Mg(B_6O_7(OH)_6).2H_2O$].

FT-IR spectra of synthesized minerals are given in Fig. 9. The proper characteristic vibrations are obtained at the mole ratio of 1:1 (Fig. 9 (a)), which is compatible with XRD results. According to the results minor changes are seen in the band values of characteristic peaks at varying mole ratios. This situation could be explained with the same formation of major phase in each experiment.

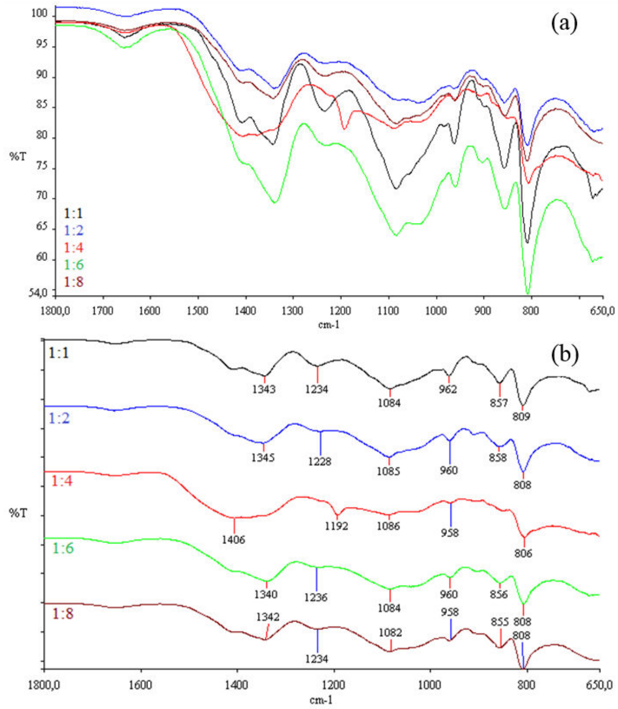

Fig. 9 FT-IR spectra of products (a) overlaid, (b) splitted

In Fig. 9 (b), the peaks at the band values of between 1406 and 1340 cm^{-1} may be explained with the asymmetric stretching of three coordinate boron and oxygen ($B_{(3)}$-O). Bending of B-O-H atoms could be seen at the band values between 1236 and 1192 cm^{-1}. The peaks around 1085 cm^{-1} are the asymmetric stretching of four coordinate boron and oxygen ($B_{(4)}$-O). The symmetric stretching of three coordinate boron and oxygen ($B_{(3)}$-O) is also seen at the band values from 962 to 855 cm^{-1}. Lower peaks value than 810cm^{-1} can be explain with the bending of three coordinate boron ($B_{(3)}$–O).

IV. Conclusion

The novelty of this research is the usage of non-traditional resources and methods for the magnesium borate mineral synthesis. By using in synthesis process as a raw material, magnesium wastes are evaluated. Thus, this kind of evaluation may help the problem of waste storage.

In these experiments it is seen that the usage of magnesium wastes in synthesis process is possible. Form the XRD results, the products are identified as mixtures of magnesium borate hydrates. In all experiment, the major phase is Mcallisterite mineral.

Obtained characteristic vibrations from FT-IR analysis are compatible with the literature and our previous studies [12], [23].

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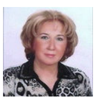

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