Asian Journal of Chemistry; Vol. 26, No. 18 (2014), 6033-6038

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2014.16504

Neutron Permeation Properties and Characterization of Synthesized Non-Hydrated Magnesium Borate Minerals

AZMI SEYHUN KIPCAK[1], EMEK MOROYDOR DERUN[1,*], FATMA TUGCE SENBERBER[1], OZGUL DERE OZDEMIR[1], DERYA YILMAZ BAYSOY[2] and SABRIYE PISKIN[1]

[1]Department of Chemical Engineering, Yildiz Technical University, Istanbul, Turkey
[2]Department of Physics, Mimar Sinan Fine Arts University, Istanbul, Turkey

*Corresponding author: Fax: +90 212 3834725; Tel: +90 212 3834776; E-mail: moroydor@gmail.com

Received: 9 October 2013; *Accepted*: 26 March 2014; *Published online*: 1 September 2014; AJC-15848

Magnesium borates are excellent materials due to their thermal and mechanical properties. In this study, the thermal (solid-state) synthesis was used for the production of non-hydrated magnesium borate minerals. In the X-ray diffraction results of thermal synthesis, Kotoite (K) "01-075-1807, $Mg_3(BO_3)_2$", Suanite (S) "01-086-0531, $Mg_2(B_2O_5)$" and (MgB^1) "00-031-0787, MgB_4O_7" and (MgB^2) "01-073-2232, $Mg_2B_2O_5$" were produced. Higher XRD scores were seen at the molar ratios of 3:2 and 1:1. Materials, XRD scores increased with increasing temperature and time. Molar ratios, reaction temperature and time for the best crystal magnesium borate materials production were determined as 3:2-1:1, 1000 °C and 240 min. Products at the highest XRD scores were subjected to neutron permeability analyses. Neutron permeability decreased with increasing thickness of the material. Increase of molar ratio of the raw materials contributed to the neutron permeability of product. The lowest values of total macroscopic cross section and neutron permeability have been found for 3:2 of $MgO:H_3BO_3$ ratio and 1.25 cm thickness.

Keywords: Magnesium borate, Microstructure, Neutron capture cross section, Radiation shielding, Solid state synthesis, Spectroscopy.

INTRODUCTION

Boron minerals, which are abundantly present in Turkey holds about 72 % of their reserves with the largest share, have been investigated for decades all over the world[1]. Metal borates, which are a member of notable ceramic materials, are useful additives in industry due to their features such as great mechanical properties, good chemical resistance and low density, as well as low thermal expansion coefficient. Magnesium borate minerals, which are a sub-class of metal borate minerals, have excellent potential in the development of thermo-luminescence phosphor materials, detergents composition, energy conversion and storage systems, production of superconducting materials, whisker-reinforced composites and reducing friction additives. At the same time, they can be used in the production of-materials against-neutron and γ-radiation due to their high content of boron[2-5].

Production of non-hydrated magnesium borates has been an interesting topic for a decade. Dosler *et al.*[2] synthesized single-phase $Mg_3B_2O_6$ and $Mg_2B_2O_5$ ceramics by solid-state reaction techniques by using the raw materials of MgO and B_2O_3. At the end of the experiments, it was seen that $Mg_2B_2O_5$ and $Mg_3B_2O_6$ were formed at temperatures ranging between 1250-1280 °C, respectively[2]. In another study on thermal synthesis, powder of $Mg(BO_2)_2{\cdot}2H_2O$ was used as the raw material for the synthesis of monoclinic $Mg_2B_2O_5$ between 1000 and 1300 ºC with a heating rate of 10 ºC/min under the pressure of 0.1 Pa[4]. Zhihong and Mancheng[6] prepared $Mg_3B_2O_6$ nanobelts with the mixture of B and MgO at the mole ratio of 1:1, under the mixture of Ar/H_2O atmosphere. The mixture of B and MgO powders was heated to 1100 °C and held at this temperature for 1.5 h. Single-crystalline magnesium borate $Mg_2B_2O_5$ nano-rods, were obtained *via* a simple route that depended on the sintering process of mixed powders containing $Mg(OH)_2$ and H_3BO_3 at the temperature of 900 °C for 3 h and then milling process was applied. The nanorods had the lengths up to a few micrometers[7]. Kipcak *et al.*[8] sintered the mixture of magnesium oxide and periclase at 800 °C and this showed that transformation began but temperature was insufficient for full conversion process.

All previous studies focus on the use of boron as an additive material for neutron shielding. Korkut *et al.*[9] studied the fast neutron shielding properties of MgB^2, $NaBH_4$ and KBH_4[9]. Buiyan and Ahmet[10] synthesized a shield material, called poly-boron, by adding boron into a matrix of polyethylene. Gwaily *et al.*[11] used boron carbide and natural rubber (40 HAF/NR) to create-thermal neutron radiation shielding. Their experimental results showed that the permeability decreased linearly

as the thickness of the sample increased. In the study of Adib and Kilany, as a thermal neutron filter, element bismuth instead of lead was investigated[12]. Singh *et al.*[13] produced PbO-B_2O_3 and Bi_2O_3-PbO-B_2O_3 shield materials at different compositions. Derun and Kipcak[14] studied the neutron absorption and transmission properties of sodium and calcium borates. According to their experiments, specifically kurnakovite was determined to yield the lowest neutron permeability value and therefore, the use of these materials for neutron shielding would be suitable. There haven't been any papers regarding the neutron permeability of magnesium borate minerals.

As it is seen in the literature, non-hydrated magnesium borates were produced at higher temperatures than 900 °C and all these studies needed the milling process for a long time. Amorphous products were obtained or sufficient conversions were not achieved. In these studies, temperature effect was studied. However, the effects of parameters such as reaction time and molar ratio of reactants were not clearly examined. Although the feature of neutron and γ-radiation absorbance of boron is known in literature. Compared with the previous studies, the novelty of this paper is investigating the neutron permeation of magnesium borate minerals. In this study, it is aimed to synthesize products at higher XRD scores. The effect of magnesium borate minerals' XRD scores on neutron permeability was also examined.

EXPERIMENTAL

Preparation and identification analysis of raw materials: Magnesium oxide and boric acid were supplied form Merck Chemicals and Kirka Boron Management Plant in Eskisehir, respectively, were selected as raw materials. Magnesium oxide was used without pretreatment and boric acid was crushed, grinded and sieved under 75 microns. Identification analysis of components was made by Philips PANanalytical X-Ray Diffraction. X-rays were produced from a CuK_α tube at 45 kV and 40 mA.

Reaction parameters of production process: To investigate the effect of molar ratio of raw materials, magnesium oxide and boric acid were mixed and pressed with different molar ratios of MgO/H_3BO_3. Manfred OL57 was used for the pressing operation. These ratios were selected as 2:1, 3:2, 1:1 and 1:2. To search the effect of reaction temperature, calcination temperatures were determined as 900 and 1000 °C. In the synthesis process, ceramic crucibles were used with a heating rate of 10 °C/min at high temperature furnace of Protherm MOS180/4. To determine the effect of reaction time, calcination processes were applied for 60 and 240 min at the determined temperatures. The final products were milled in an agate mortar.

Characterization of synthesized minerals: After the synthesis of non-hydrated magnesium borates, X-rays were produced from a CuKα tube at 45 kV and 40 mA for XRD analyses.

For the characterization analysis of products, Perkin Elmer Brand FT-IR with Universal Attenuated Total Reflectance (ATR) sampling accessory-Diamond/ZnSe crystal was used. Measurement range was selected as 1800-650 cm^{-1}. After FT-IR analysis, Perkin Elmer Brand Raman spectrometer was used for further analysis. For Raman spectroscopy, the exposure time was set to 4 sec and number of exposures was set to 4. Measurement range was selected as 1800-250 cm^{-1} and data interval was selected as 2 cm^{-1}. In addition to characterization analyses, SEM analysis was applied for the surface morphology. CamScan Apollo 300 field-emission SEM was used and experiments were conducted at 20 kV. Detector used was back scattering electron (BEI) and magnification was set to 5000x.

After the solid-state synthesis, boron oxide (B_2O_3) contents of the minerals were determined with the titration method. 1 g of each product was dissolved in 3 mL of 37 % HCl and titrated with NaOH. Pure H_3BO_3 at the same conditions was used as the reference material.

Neutron permeation of synthesized minerals: Synthesized minerals (10, 15 and 25 g) were mixed with 10 % Wax® by weight and then pelleted in three different thicknesses which were measured as 0.55, 0.75 and 1.25 cm. Neutron permeation experiments were carried out by Am-Be neutron flux with the activity of 74GBq from a source located within Howitzer the Çekmece Nuclear Research and Training Center, Turkey. Fast neutrons, which produced by a neutron source, have the average energy value of 4.5 MeV and maximum energy level of 12 MeV. BF_3 neutron detector with diameter of 2.54 cm and length of 28 cm was used during the experiments. Since the minerals were placed at the exit of the source beam collimation component was not used. Neutron permeability experimental setup is schematized in Fig. 1. The three pellets, with different thicknesses, were exposed to neutrons in the Howitzer device for 5 min and three parallel experiments were conducted.

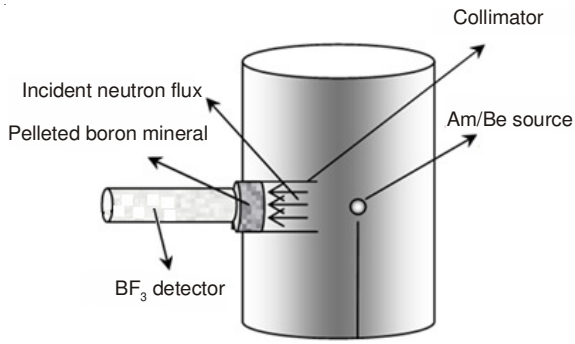


Fig. 1. Schematic diagram of neutron permeability experimental setup

The neutron permeability is determined from I/I_0 and x, where I and I_0 are the transmitted and incident neutron fluxes, respectively and x is the thickness of the mineral[15]. To discuss about neutron shielding properties of the synthesized minerals, values of total macroscopic cross section (Σ_t) can be calculated from Beer-Lambert Law in equation:

$$\frac{I}{I_0} = e^{-\Sigma_t x}$$

Total macroscopic cross sections were calculated for each thickness and their average values were calculated.

RESULTS AND DISCUSSION

Characterization results of magnesium oxide and boric acid: XRD patterns of magnesium oxide and boric acid are

shown in Fig. 2. It is known that boric acid loses its water at higher temperatures and turn into boron oxide (B_2O_3). According to XRD results, raw materials were found with refer ence codes and of scores of "01-087-0651" and 78 for MgO and "01-073-2158" and 62 for H_3BO_3. After boric acid was heated, it transformed to boron oxide which has reference code and score of "00-006-0297" and 42, respectively.

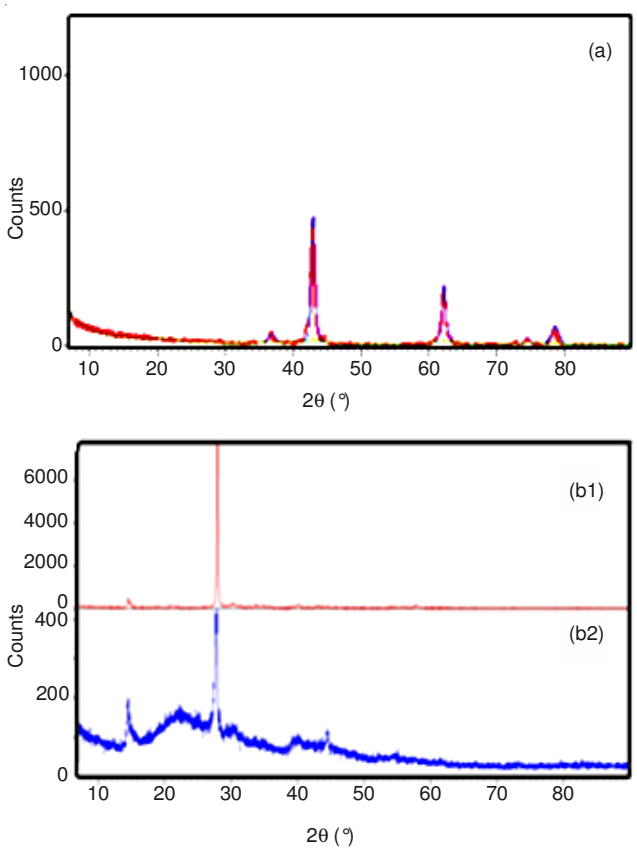


Fig. 2. XRD patterns of (a) MgO, (b1) H_3BO_3, (b2) B_2O_3

Characterization results of synthesized magnesium borate minerals: XRD results of synthesized magnesium borates and scores of these minerals are given in Table-1. At the end of the XRD analysis, Kotoite (K) "01-075-1807, $Mg_3(BO_3)_2$", Suanite (S) "01-086-0531, $Mg_2(B_2O_5)$" and the other forms of magnesium borates (MgB^1) "00-031-0787, MgB_4O_7" and (MgB^2) "01-073-2232, $M_2B_2O_5$" were identified. Phase changes with the varying parameter are given in Fig. 3.

TABLE 1
XRD RESULTS OF PRODUCED MATERIALS

Temp.		900 °C				1000 °C			
Time		60 min		240 min		60 min		240 min	
		Code	Score	Code	Score	Code	Score	Code	Score
Molar Ratio	2:1	K	56	K	55	K	52	K	62
		S	20	S	26	MgB^2	36	MgB^2	36
		MgB^1	17	MgB^1	22				
	3:2	K	56	K	60	K	57	K	62
		S	26	S	22	MgB^2	41	MgB^2	41
		MgB^1	10	MgB^1	25				
	1:1	K	56	K	48	K	47	K	47
		S	33	S	32	MgB^2	46	MgB^2	46
		MgB^1	16	MgB^1	21				
	1:2	K	47	K	36	K	32	K	27
		S	23	S	25	MgB^2	37	MgB^2	46
		MgB^1	25	MgB^1	28				

Effects of changing parameters to XRD scores can be seen in Table-1 and the crystallographic data obtained from XRD are given in Table-2. For the experiments made to investigate the change of reaction temperature, the XRD scores of synthesized products increased with increasing temperature where a perfect crystal score is equal to 100. For the experiments in which the reaction time changed, the XRD scores of synthesized products increased with extended time. According to XRD scores in the scan of the molar ratio of raw materials, it can be said that the most suitable molar ratios values are 3:2

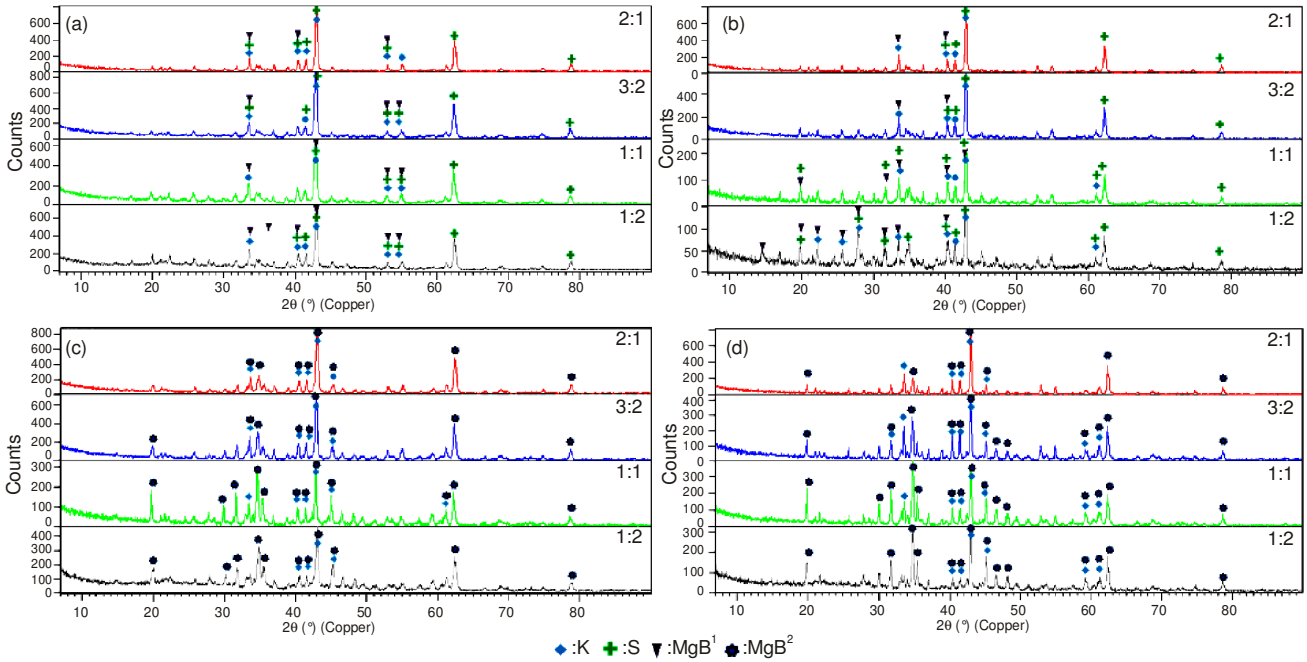


Fig. 3. XRD patterns of synthesized products (a) 900 ºC-60 min, (b) 900 ºC-240 min, (c) 1000 ºC-60 min and (d) 1000 ºC-240 min

TABLE-2
CRYSTALLOGRAPHIC DATA OF SYNTHESIZED DEHYDRATED MAGNESIUM BORATES

Mineral name	Kotoite	Suanite	Magnesium borate	Magnesium borate
PDF no.	01-075-1807	01-056-0531	00-031-0787	01-073-2232
Chemical formula	$Mg_3(BO_3)_2$	$Mg_2(B_2O_5)$	MgB_4O_7	$Mg_2B_2O_5$
Molecular weight (g/mol)	190.53	150.23	179.54	150.23
Crystal system	Orthorhombic	Monoclinic	Orthorhombic	Anorthic
Space group	Pnmn	P21/c	Pbca	P-1
a (Å)	5.398	9.1970	5.896	6.187
b (Å)	8.416	3.1228	13.729	9.219
c (Å)	4.497	12.3030	7.956	3.119
α (°)	90.00	90.00	90.00	90.40
β (°)	90.00	104.26	90.00	92.13
γ (°)	90.00	90.00	90.00	104.32
z	2.00	4.00	8.00	2.00
Density (g cm^{-3})	3.10	2.91	2.54	2.90

and 1:1. When MgO/H_3BO_3 ratios are 3:2 and 1:1, Kotoite and MgB^2 are major components.

Since the molar ratios of 3:2 and 1:1 selected because of their high XRD crystal scores, FT-IR and Raman spectrum are given in Figs. 4 to 7.

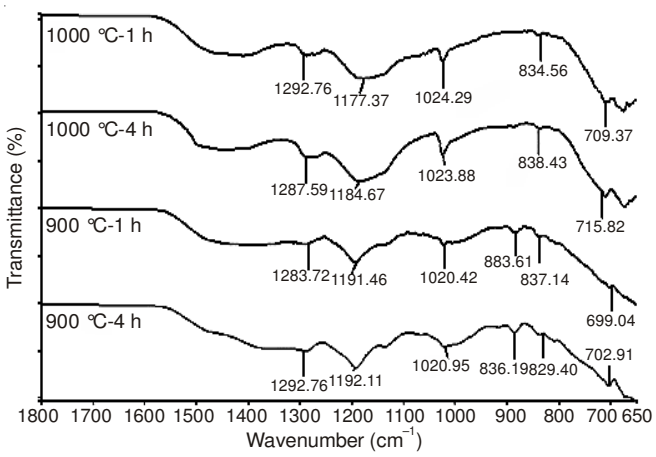


Fig. 4. FT-IR spectra of product for $MgO:H_3BO_3$ ratio of 3:2 at different reaction temperatures and times

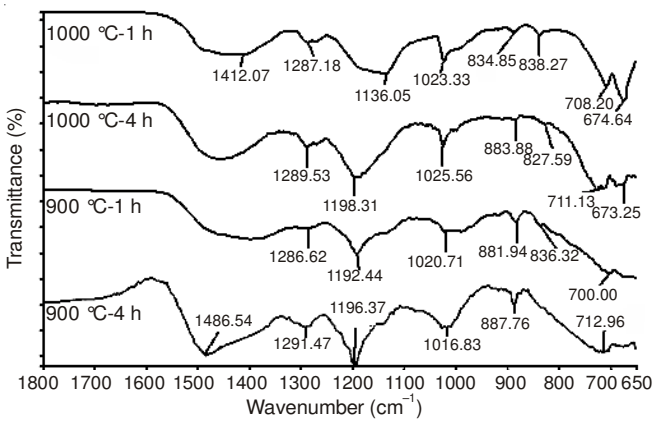


Fig. 5. FT-IR spectra of product for $MgO:H_3BO_3$ ratio of 1:1 at different reaction temperatures and times

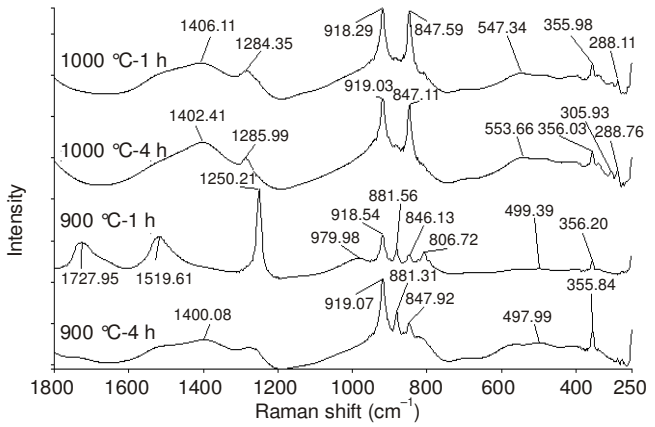


Fig. 6. Raman spectra of product for $MgO:H_3BO_3$ ratio of 3:2 at different reaction temperatures and times

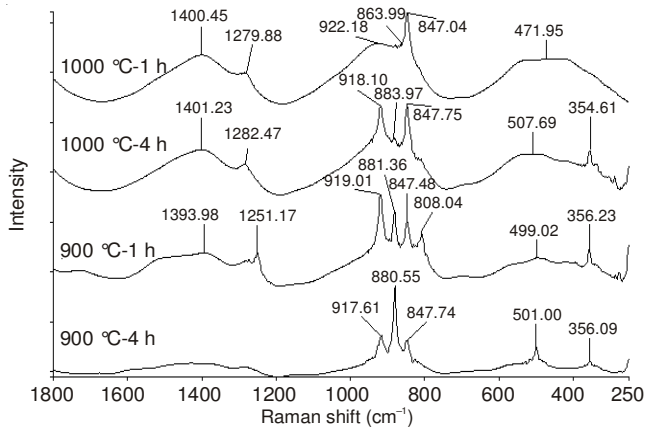


Fig. 7. Raman spectra of product for $MgO:H_3BO_3$ ratio of 1:1 at different reaction temperatures and times

In the FT-IR spectra of synthesized magnesium borate minerals, the main characteristic peak values are seen in Figs. 4 and 5. According to FT-IR spectra, asymmetric stretching of $B_{(3)}$-O can cause the first two peaks of the synthesized minerals with the band values between 1486.54 and 1283.72 cm^{-1}. With the band values between 1198.31 and 1016.83 cm^{-1}, peak 3 and 4 may arise from the asymmetric stretching of $B_{(4)}$-O in the structure of magnesium borates. Peak 5 and 6 which had band values changing between 887.76 and 827.9 cm^{-1}, can be explained with the symmetric stretching of $B_{(3)}$-O. At the end of the spectrum, last peaks between 715.82 and 673.25 cm^{-1}, peaks 7 and 8, are results of the bending of three coordinate boron bands.

According to Raman spectra, asymmetric stretching of $B_{(3)}$-O might cause first two peaks of produced magnesium borate minerals, with band values between 1727.95 and 1250.21 cm^{-1}. Third and fourth peaks of these products, which are in between 979.98 and 806.72 cm^{-1}, are due to the symmetric stretching of $B_{(3)}$-O. Last peaks with the band values below 800 cm^{-1} are based on symmetric stretching of $B_{(4)}$-O.

According to the identification and characterization results of products, 3:2 and 1:1 molar ratios and 240 min of reaction time are ideal for synthesis due to higher XRD scores. Thus, SEM analysis was applied to these products for varying temperatures. Surface images of synthesized materials are shown in Fig. 8. According to Fig. 8 for the molar ratio of 3:2 and 1:1 with a magnification of 5000x, a great percentage of

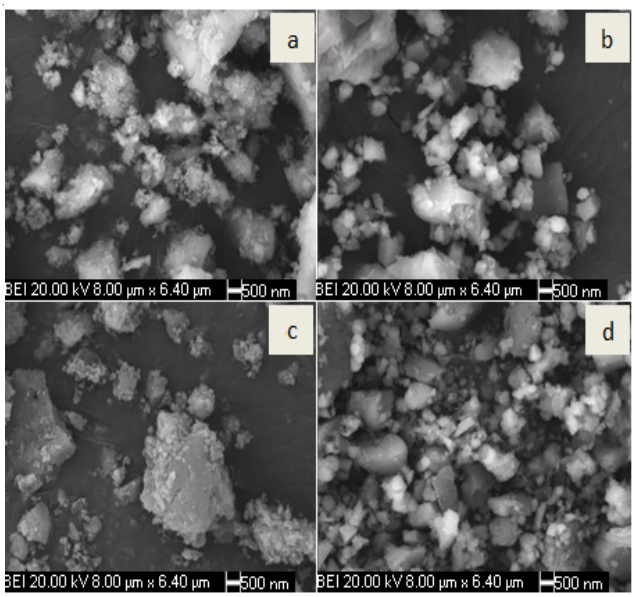


Fig. 8. SEM images of products synthesized at the parameters of $MgO:H_3BO_3$ ratio; (a) 900 °C-3:2, (b) 1000 °C-3:2, (c) 900 °C-1:1, (d) 1000 °C-1:1

magnesium borate minerals were crystallized in rectangular shapes. In addition, the synthesized crystals become smaller with the increasing temperature. Particle sizes of the crystals of synthesized materials were found approximately between 585 nm to 1.6 µm.

The boron oxide contents of synthesized materials are seen in Table-3. In literature, the boron content of Kotoite and Suanite are 36.54 and 46.34 %, respectively[16]. Boron oxide contents of the synthesized materials were changed between 25.46 ± 0.27 and 52.86 ± 0.27 %. Higher boron contents of the products can be explained with the excess boric acid at the molar ratio of 1:2. In similar way, lower boron contents of the products can be explained with the excess magnesium oxide and insufficient conversion to magnesium borate structure at the molar ratio of 2:1.

TABLE-3
BORON OXIDE CONTENT OF SYNTHESIZED MATERIALS

Reaction Temperature: 900 °C	Molar Ratio	B_2O_3 %	Reaction Temperature: 900 °C	Molar Ratio	B_2O_3 %
	2:1	38.97±0.14		2:1	25.46±0.27
	3:2	40.42±0.82		3:2	28.67±0.41
	1:1	47.13±0.14		1:1	30.80±0.69
	1:2	52.86±0.27		1:2	33.43±0.27

Neutron permeability: Neutron permeability decreases with increasing thickness of the material[15]. Neutron permeability and macroscopic cross section values of the synthesized magnesium borate minerals are given in Table-4. According to the results for each thickness ratio of I/I_o was higher at the molar ratio for 1:1. The lowest values of total macroscopic cross section and neutron permeation were found for a molar ratio of 3:2. Thus means that synthesized magnesium borate minerals with a molar ratio of 3:2 is more suitable for neutron shielding.

In the experiments, it is seen that thicknesses in materials and molar ratio are important for neutron permeability properties

TABLE-4
NEUTRON PERMEABILITY VALUES OF SYNTHESIZED MINERALS

Molar ratio	Thickness (cm)	I/I_o	Σ_t (cm^{-1})
3:2	0.55	0.6469	0.3728
	0.75	0.6187	
	1.25	0.5500	
1:1	0.55	0.7375	0.4181
	0.75	0.7156	
	1.25	0.6750	

of products. In addition to the effect of thickness, neutron permeation decreased with increasing molar ratio of raw materials in products.

Conclusion

Boron minerals are used as additive compounds in shielding materials. There is not study in literature on shielding properties of magnesium borate minerals, although neutron and γ-permeability is known as a feature of boron. In literature, no study is reported about the crystal scores effects of the synthesized materials' neutron permeabilities. In this study, the aim was to determine the neutron permeability of non-hydrated magnesium borate and the effect of XRD crystal scores on shielding features.

In first stage, the influence of thermal production process parameters on synthesis, characterization and crystal structure of materials were studied by the techniques of XRD, FT-IR, Raman and SEM. The investigated parameters were reaction time and molar ratio of the raw materials.

According to XRD scores, crystallinity features were found to change with molar ratio. In all reaction temperatures, the highest XRD scores were obtained for molar ratios of 3:2 and 1:1. Experiments at 900 °C showed that the production process needed higher temperatures. With increasing reaction temperature from 900 to 1000 °C, higher XRD scores were determined for synthesized materials. In a similar way, a suitable reaction time could be decided as 240 min. According to the identification and characterization results of products, the products which have the highest XRD scores was synthesized at a reaction temperature of 1000 °C, reaction time of 240 min and molar ratios of 3:2-1:1. In these products, Kotoite $[Mg_3(BO_3)_2]$ and MgB^2 (MgB_4O_7) were the major phases in the products which synthesized at the ratio of $MgO:H_3BO_3$ 3:2 and 1:1, respectively. FT-IR and Raman results of products showed that the peaks of synthesized materials were suitable with the characteristic peaks of non-hydrate boron minerals in literature[6,15,17]. The characters of synthesized material were less affected from changing of experimental parameters.

From the surface morphology of the synthesized materials, it was seen that particles were shaped more rectangular and smaller with increasing temperature. According to the measurements made by SEM, particle sizes were changed between 586 nm 1.6 µm.

Neutron permeability results of the chosen products (at 1000 °C reaction temperature, 240 min reaction time and 3:2-1:1 molar ratios) showed that the ratio of I/I_o changed with thickness and molar ratio of raw materials in the synthesis process. When thickness of the material was higher, the neutron

permeability became lower. In a similar way, total macroscopic cross section decreased with increasing material thickness. Although it does not have a tremendous impact, increase on molar ratio of MgO/H_3BO_3, which was a major factor for the structure of the product had a positive effect on neutron permeability of product.

Since the XRD crystal scores of the boron source contributed to the shielding properties, XRD crystal scores are important. In conclusion, the optimum parameters for the synthesis of non-hydrated magnesium borate minerals were determined for the use in neutron shielding purpose.

ACKNOWLEDGEMENTS

The authors expressed their deepest gratitude and appreciation to Dr. Ekin Kipcak for her valuable help.

REFERENCES

1. T.R. Prime Ministry SPO, Chemical Industry Private Expertise Commission, Boron Operations Group Report: Ninth Development Plan (2007-2013), Turkey (2006).
2. U. Dosler, M.M. Krzmanc and D. Suvorov, *J. Eur. Ceram. Soc*., **30**, 413 (2010).
3. X. Tao and X. Li, *Nano Lett*., **8**, 505 (2008).
4. Y. Zeng, H. Yang, W. Fu, L. Qiao, L. Chang, J. Chen, H. Zhu, M. Li and G. Zou, *Mater. Res. Bull*., **43**, 2239 (2008).
5. W. Zhu, G. Li, Q. Zhang, L. Xiang and Z. Zhu, *Powder Technol*., **203**, 265 (2010).
6. L. Zhihong and H. Mancheng, *Thermochim. Acta*, **403**, 181 (2003).
7. E.M. Elssfah, A. Elsanousi, J. Zhang, H.S. Song and C. Tang, *Mater. Lett*., **61**, 4358 (2007).
8. A.S. Kipcak, F.T. Senberber, E.M. Derun and S. Piskin, CEAM, Barcelona, 14-28 November (2011).
9. T. Korkut, A. Karabulut, G. Budak and H. Korkut, *J. Radioanal. Nucl. Chem*., **286**, 61 (2010).
10. S.I. Buiyan and F.U. Ahmet, *Health Phys*., **57**, 819 (1989).
11. S.E. Gwaily, M.M. Badawy, H.H. Hassan and M. Madani, *Polym. Test*., **21**, 129 (2002).
12. M. Adib and M. Kilany, *Radiat. Phys. Chem*., **66**, 81 (2003).
13. N. Singh, K.J. Singh, K. Singh and H. Singh, *Nucl. Instrum. Methods*, **225**, 305 (2004).
14. E.M. Derun and A.S. Kipcak, *J. Radioanal. Nucl. Chem*., **292**, 871 (2012).
15. A.S. Kipcak, P. Gurses, E.M. Derun, N. Tugrul and S. Piskin, *Energy Convers. Manage.*, **72**, 39 (2013).
16. J.W. Anthony, R.A. Bideaux, K.W. Bladh and M.C. Nichols, Handbook of Mineralogy, Mineralogical Society of America, Chantilly, VA 20151-1110, USA.
17. J. Yongzhong, G. Shiyang, X. Shuping and L. Jun, *Spectrochim. Acta A*, **56**, 1291 (2000).