International Journal of Trend in Scientific Research and Development (IJTSRD)
Volume: 3 | Issue: 3 | Mar-Apr 2019 Available Online: www.ijtsrd.com e-ISSN: 2456 - 6470

Synthesis and Characterization of Magnesium Borate via Sol-Gel Method and Electrospinning Method

Esra Nur Doğana[1], Fatih Demir[2]

[1]Eti Maden İşletmeleri, Ankara, Turkey
[2]Department of Chemical Engineering, Ataturk University Engineering, Ezurum, Turkiye

How to cite this paper: Esra Nur Dogana | Fatih Demir **"Synthesis and Characterization of Magnesium Borate via Sol-Gel Method and Electrospinning Method"** Published in International Journal of Trend in Scientific Research and Development (ijtsrd), ISSN: 2456-6470, Volume-3 | Issue-3, April 2019, pp.129-134, URL: http://www.ijtsrd.com/papers/ijtsrd21662.pdf

IJTSRD21662

ABSTRACT

The sol-gel and electrospinning techniques were used to prepare the magnesium borate/polyvinyl alcohol composite. The fibers of magnesium borate about 150 nm diameters, were synthesized from the inorganic-organic composite fibers by high temperature calcination process. The synthesized magnesium borate nanofibers were structurally investigated by thermogravimetric/differential thermal analysis (TG/DTA), Fourier transform-infrared spectroscopy (FT-IR), X-ray diffractometry (XRD) and Scanning electron microscopy (SEM), respectively. Due to the Mg modification of the B_2O_3 network, incomplete crystallization of the samples was observed when heat treated at 800 °C. But, completely crystalline fibers were obtained after calcined at 1200 ° C.

KEYWORDS: *Sol-gel method; Electrospinning; Magnesium borate/polyvinyl alcohol composite*

1. INTRODUCTION

Nanotechnology science deals with the design and control of both nanosized shapes and dimensions, and the structure, system, production, characterization and its applications. The one-dimensional nanoscale materials such as nanofibers, nanorods and nanowires have gained considerable attention in recent years owing to the technological applications [1-5]. Nanofiber materials are widely used for nanotechnology applications because of their properties which are different from macro size due to their properties such as conductivity, reactivity and strength for nanotechnology applications. Nanosize materials display superior chemical, mechanical, optical, electronicand magnetic properties for a wide range of applications because of their small dimensions and high surface areas [7-9].

Magnesium borates exist the minerals of economic importance like hydroboracite ($CaMgB_6On\text{-}6H_2O$) and szaibelyite ($Mg_2B_2O_5\text{-}H_2O$) structure in nature. They are synthesized in the forms of $MgO.B_2O_3.nH_2O$, $2MgO\text{-}3B_2O_3.nH_2O$ etc. [10-14]. Magnesium borates are important a ceramic material that shows excellent mechanical and thermal properties such as the required catalysts for the conversion of hydrocarbons. Various methods for the preparation of magnesium borates are used the thermal syntheses, microwave heating or chemical vapor deposition methods, including solid state reactions, co-precipitation, mechano-chemical complexation and electrospinning method [15-18].

In the recent years, Electrospinning is the easiest technique utilized in production of functional nanofibers such as alumina, silica, magnesium borates etc. This technique has been used to be simple to obtain metal oxide composites possessing small-diameter particles high specific surface area, which are useful in a variety of applications [19-20]. The important advantages of this technique are the ability to control with accuracy the fiber, a high aspect ratio of the products, not expensive at the laboratory scale. But, disadvantages of this method are that the method requires high voltage usually in the 10-40 kV range, only a few polymers are currently applied for preparation of organic nanofibers and the range of application of electrospun inorganic nanofibers has been limited due to their fragility after calcination and ıt is the low yield in the low flow rates are indeed required to achieve nano-scale fiber diameters [21].

In a recent work, Storti et al., the electrospinning technique for the synthesis of magnesium borate fibers investigated. They obtained the presence of fibers with diameters in the 100–300 nm range after heat treatment at 800 ◦C and 1000 ◦C [21]. In another study, a new one-dimensional

nanostructure, $Mg_3B_2O_6$ nanobelts were synthesized by thermal treating of the mixed powders of boron and magnesium oxide in the presence of H_2O vapor. Magnesium borate nanobelts were prepared by heating mixed powders of boron and MgO under flowing Ar/H_2O gases at 1100 ^oC, and typical widths of the nanobelts were obtained in the range of 100-300 nm [22]. Sevim et al. Nanofibers of PVA /nickel nitrate/silica/alümina izopropoxide/boric acid composite prepared by using sol-gel processing and electrospinning technique. As a result, By high temperature calcinations of the above precursor fibers, nanofibers of $NiO/Al_2O_3/B_2O_3/SiO_2$ composite with diameters about 500 nm were successfully obtained [23].

In this paper, we present the production of pure magnesium borate nanofibers by the calcination of inorganic composite fibers obtained through electrospinning by sol-gel method. We report a production nanofibers and characterization of magnesium borate nanofibers. This study may be useful to investigate the possibilities of commercial application of the magnesium borate nanofibers in the coming years.

2. EXPERİMENTAL

The boron source of boric acid (H_3BO_3) is retrieved from Etibank Emet Boron and Acid Factory in Turkey. The electrospinning sol-gel solutions consisted of $Mg(NO_3)_2$ (Merck,>99%), hydrochloric acid (Sigma-Aldrich, 37%), polyvinyl alcohol (PVA Mw = 240.000 g/mol, Sigma-Aldrich), ethanol (Sigma-Aldrich, >99%) and distilled water. The aqueous solution of PVA was firstly prepared by dissolving 10 g PVA powder in 100 ml distilled water stirring for 2 h at 80 °C. Then it was cooled to room temperature by stirring continued for 12 h. The gel solution was prepared by mixing ethanol, concentrated HCl and distilled water all together. The mixed solution was kept with magnetic stirring for 2h in a room temperature. In another bowl, PVA and boric acid were mixed with magnesium nitrate. Then the other solutions were added into the prepared PVA solution under stirring at a slow speed in a particular order. The pH of the medium must be below 2 because of it is prevented peptization during the formation of the sol-gel. Then the gel composite was filled in a plastic syringe (10 ml) and placed into syringe pump. A copper wire connected to a high-voltage device was attached to the plastic syringe by adjusting the angle between the fixing bar and the capillary tip. A voltage 15 kV and the feed 0.3 ml/h rate was applied to the gel. The fibers were accumulated on the aluminum foil. Measured fiber diameters were obtained on solution %10 PVA, distance 15 cm and voltage 15 kV in ideal working conditions. The fibers occurred were firstly dried at 110 °C for 2 h and then calcined in air at 800 °C and 1200 °C, standing at a heating rate of 2 °C /min for 2 h, respectively. The magnesium borate nanofibers were obtained.

DTA and TG were operated on a NETZSCH STA 449F3 thermo-processing in air at a temperature range of 0–1200 °C and thermal experiments were treated with a certain sample weight. The sample was established a platinum crucible and its dehydration was recorded at the 10 °C min^{-1} of constant heating rate under nitrogen atmosphere with 20 min of a purge time and 25 ml/min of a flow rate.

The absorbance spectra of deposited nanofibers of Magnesium borate composite on Au Plates were measured using a different angle reflection equipment in conjunction with a Perkin–Elmer Spectrum One FTIR spectroscopy in the range of 4000-400 cm^{-1} at room temperature. All the measurements were obtained with a resolution of 2 cm^{-1} and an average of 100 scans. SEM (Philips XL30 SFEG) was investigated the morphologies of the samples. SEM images were recorded using a Leco 1430 V.P. SEM instrument with 12–24 kV accelerating voltage and 130–150 pA beam current.

XRD (The thermobalance measured mass to 0.001mg, with an accuracy of ±1%.) experiments for nanofilms on nanofibers of Magnesium borate composite were measured with a Rigaku Advance Powder X-ray Diffractometer device using Cu Kα radiation (λ = 1.5405 Å), operating at 30 mA and 30 kV about a 2h range of 20–60^o. The XRD phases were identified with the help of the Joint Committee on Powder Diffraction Standards-International Center for Diffraction Data (JCPDS-ICDD).

3. RESULTS AND DISCUSSION

3.1. Differential Thermal and Thermogravimetric Analysis (DTA/TG):

The TG and DTA results are shown in Fig. 1. As seen from the DTA curve two endothermic peaks, related with the loss of absorbed water, dehydration on the side chain of polymer and degradation of remaining alkyl groups, are around 165.4 and 283.3 °C. In addition to those, the organic groups and PVA were utterly removed at 400-500 °C. As seen TG curve, the loss of sample weight was obtained about 80%. Above the temperature of 600 °C related to the formation of pure inorganic oxide in crystalline form, there is not seen any loss of weight. Equations (1), (2) and (3) describe the room temperature and thermal process, respectively;

$$7Mg(NO_3)_2 + 4H_3BO_3 + 14NaOH \rightarrow Mg_7B_4O_{13}\cdot 7H_2O(s) + 14NaNO_3 + 6H_2O \quad (1)$$

$$Mg_7B_4O_{13}\cdot 7H_2O(s) + 3H_3BO_3 \rightarrow 7MgBO_2(OH)(s) + 8H_2O \quad (2)$$

$$2MgBO_2(OH)(s) \rightarrow Mg_2B_2O_5(s) + H_2O \quad (3)$$

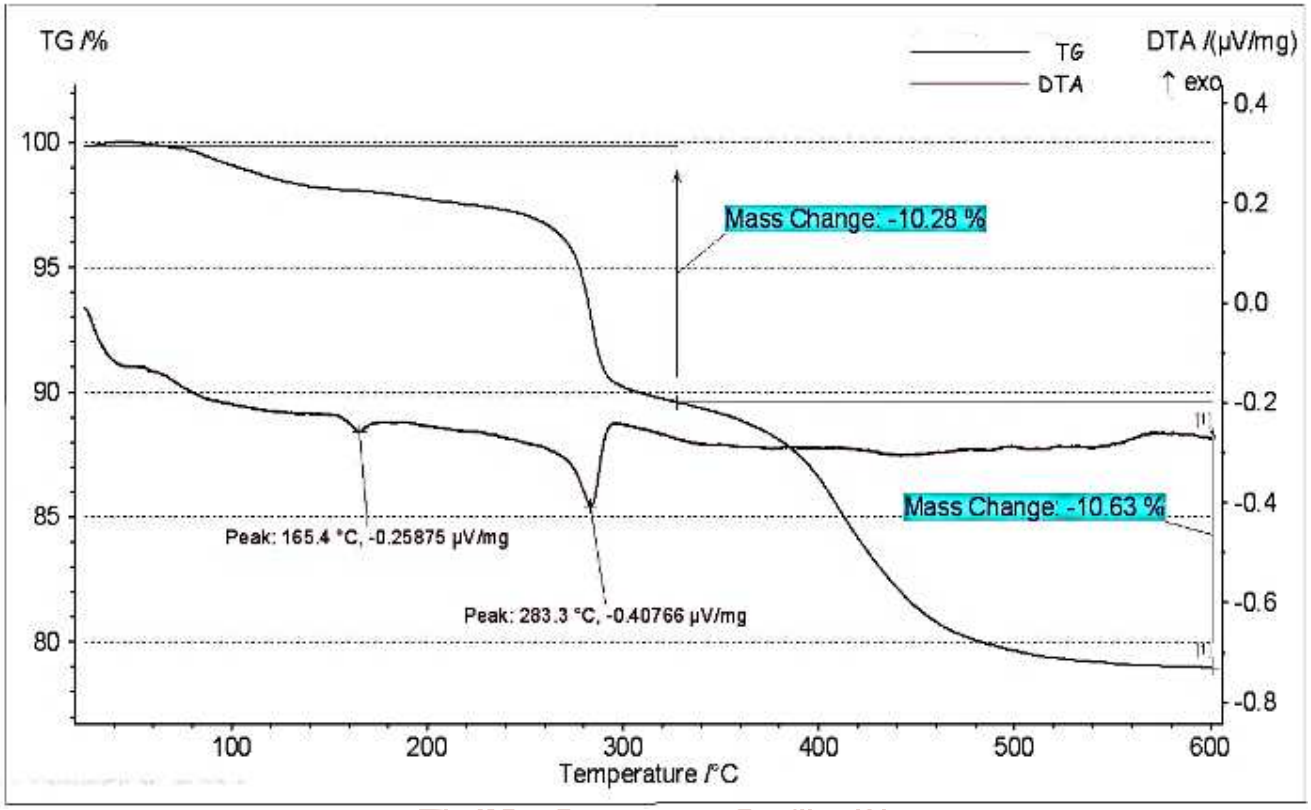

Fig.1. TG-DTA thermogravimeter for the composite fibers of the $Mg_2B_2O_5$/PVA in nitrogen atmosphere

3.2. Fourier Transform Infrared (FT-IR):

Fig. 2-3 shows the FT-IR spectra the $Mg_2B_2O_5$/PVA fibers at room temperature, and for those sintered at temperatures of 800°C and 1200°C, respectively. In Figures, the $Mg_2B_2O_5$/PVA fibers show a broad peak at 3272 cm^{-1} corresponding to H–OH stretch; and the characteristic absorption peaks at about 2916, 2624, 2021, 1655, 1325 and 1086 corresponding to vibration bands of C–C, C–H, O–H, C–O, respectively. The BO_3 in 826 cm^{-1} and 1412 cm^{-1} peaks, BO_4 in 914 cm^{-1} and 1086 cm^{-1} peaks and BOH in 1325 cm^{-1} peak is indicated the structure of bonds in Fig.2-3. In sintering, between 800 °C and 1200 °C, all peaks forming from water and organic structures almost disappeared. In addition, at these temperatures clear new peak groups, which may be associated to the formation of inorganic phase crystalline, appears at 800-1650 cm^{-1}. Thus, it may be received that these peaks over and over each other.

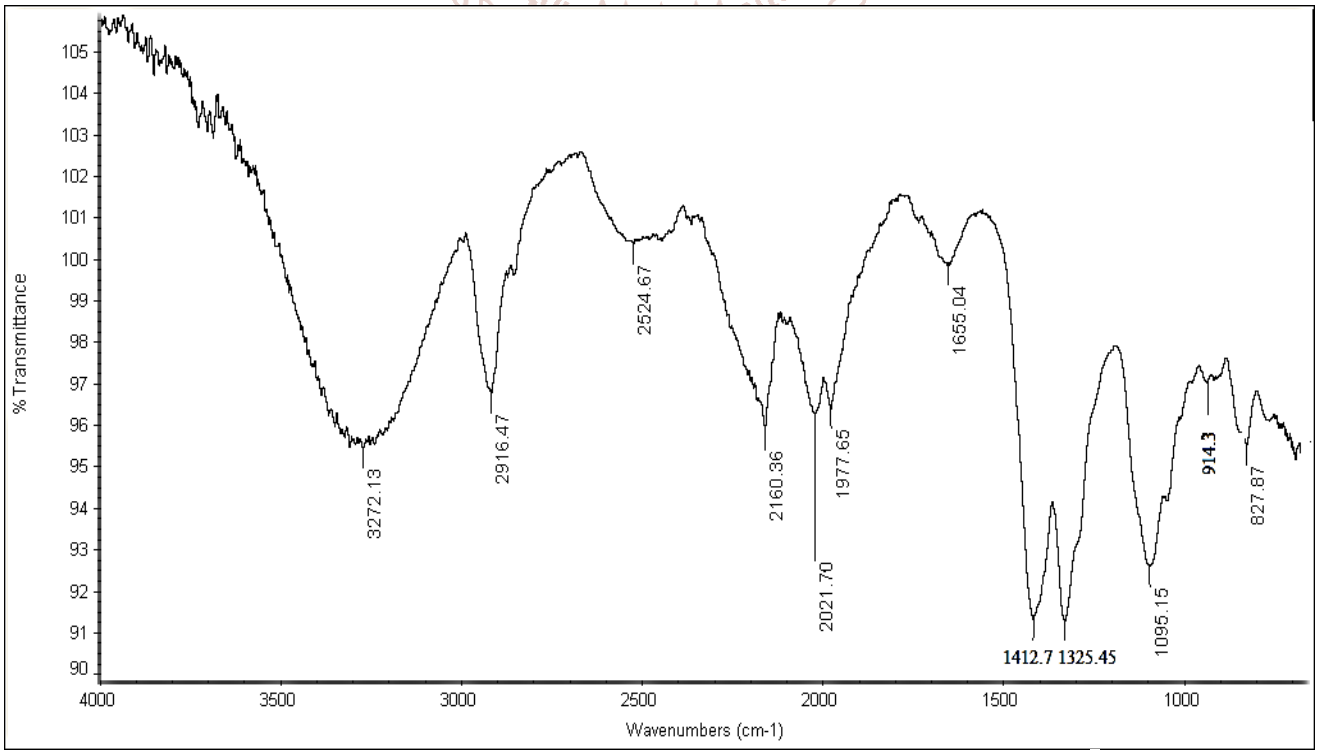

Fig.2. FT-IR spectrum analysis for the composite fibers of the $Mg_2B_2O_5$/PVA at 800 °C

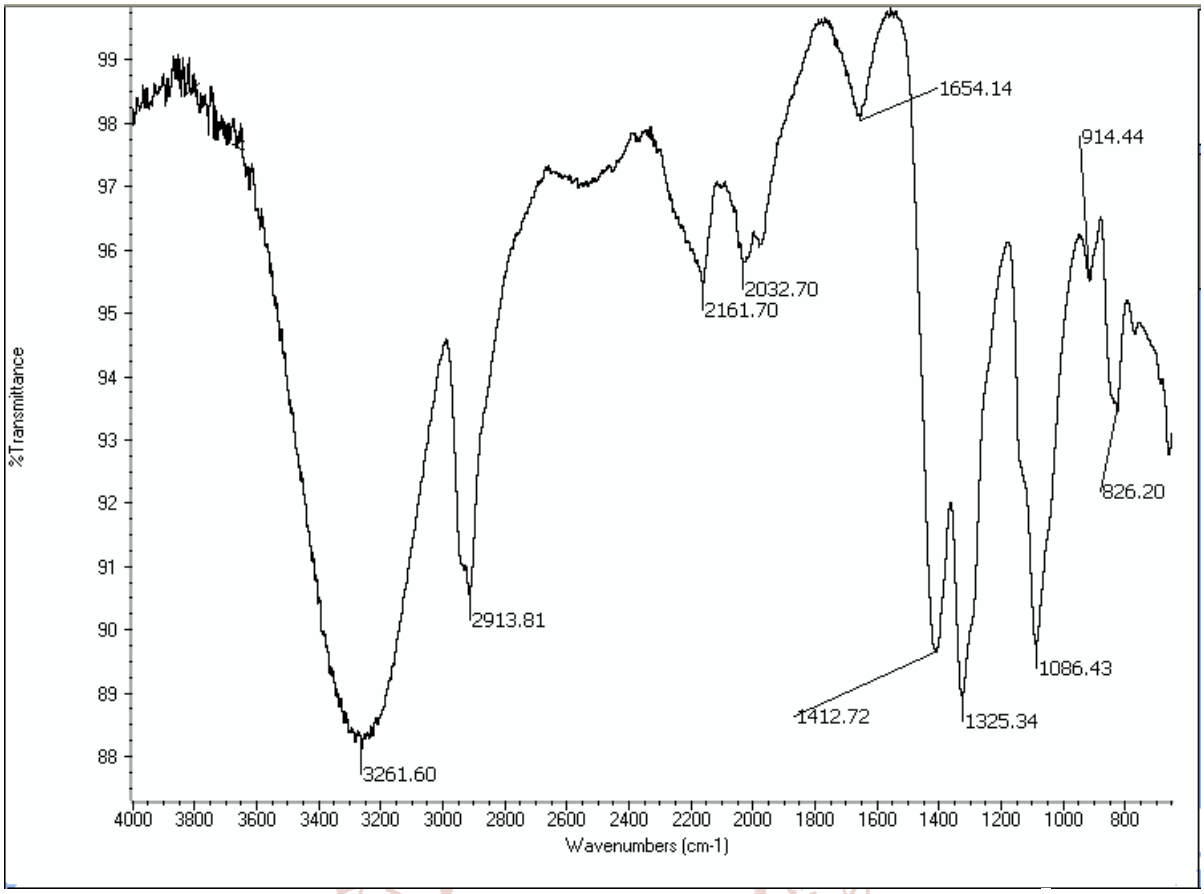

Fig.3. FT-IR spectrum analysis for the composite fibers of the $Mg_2B_2O_5$/PVA at 1200 °C

3.3. X-ray Diffraction (XRD):

Fig. 4 and 5 shows the XRD pattern of as-prepared $Mg_2B_2O_5$ nanofibers in calcination temperature at 800 and 1200 °C. All of the diffraction peaks can be indexed as a triclinic $Mg_2B_2O_5$ structure (JCPDS Card No: 83-0625). The characteristic peaks at 31.78, 35.38 and 45.2 in the spectrum can be readily corresponded to [200], [-220], [0-21], [-3 2 0], [-131] and [141] crystal planes of $Mg_2B_2O_5$. The image diffraction peaks recommend that the patterns could be well crystallized. $Mg_2B_2O_5$ nanofibers with high purity were obtained.

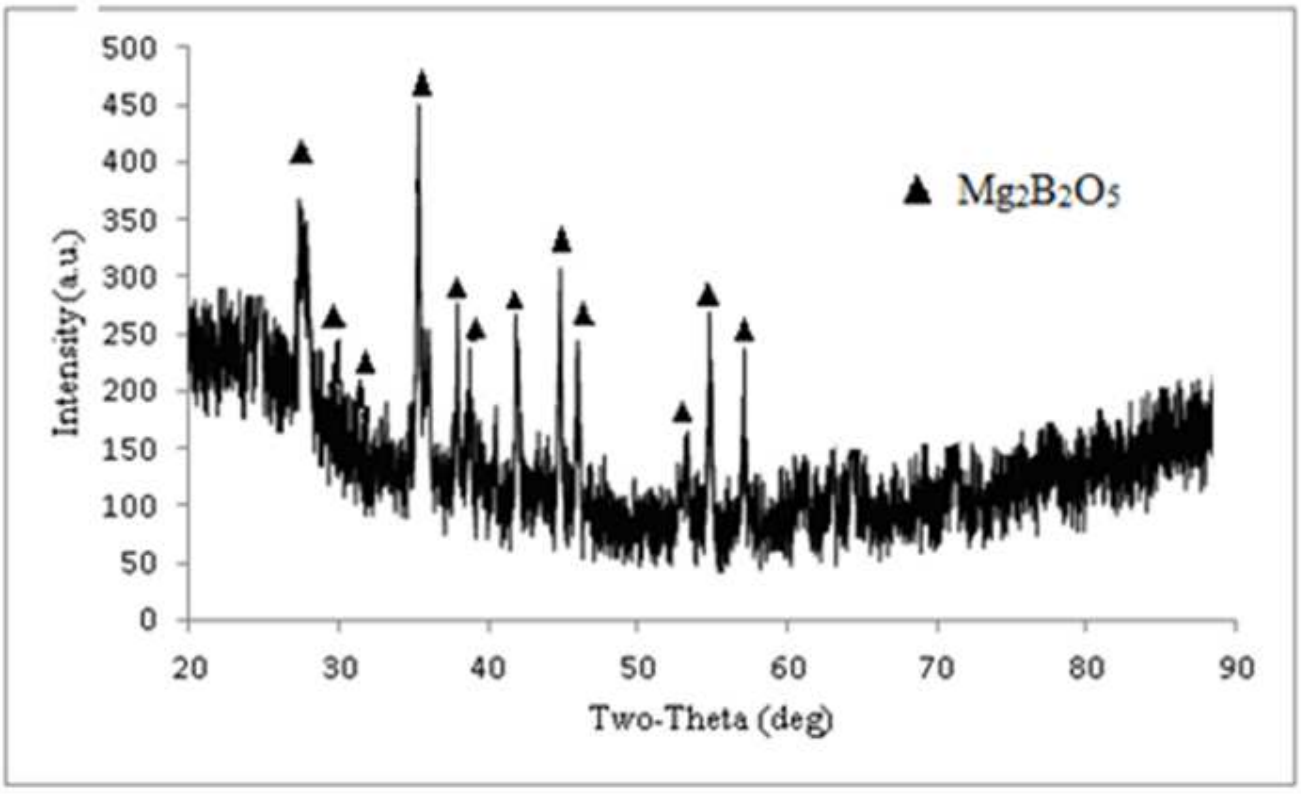

Fig.4. XRD pattern of $Mg_2B_2O_5$ nanofibers at 800 °C.

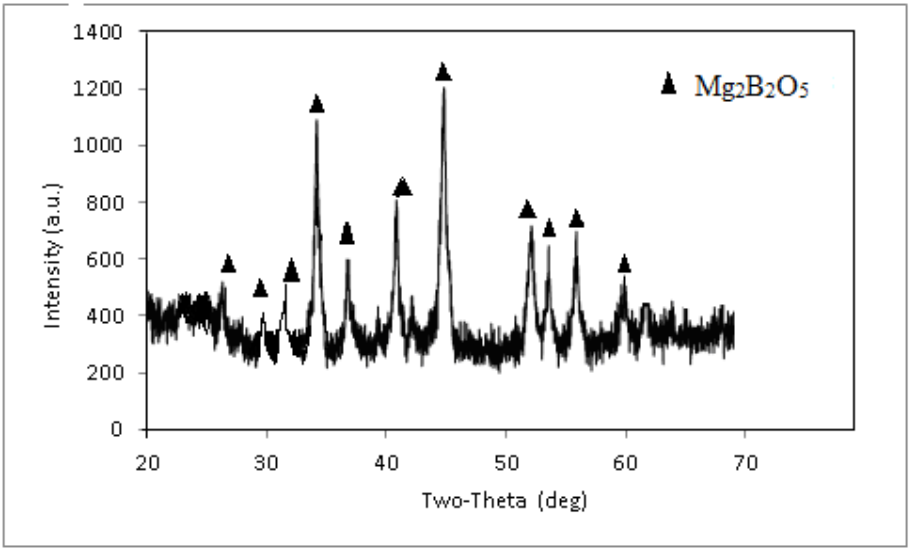

Fig.5. XRD pattern of $Mg_2B_2O_5$ nanofibers at 1200 °C.

3.4. Scanning electron microscopy (SEM):

Fig. 6-8 show before calcined, 800 °C and 1200 °C calcined, respectively. It was used ImageJ programming for particle diameters. SEM appearances of the magnesium borate before calcined are shown an irregular structure which beaded in Fig. 6. High-magnification SEM image shown in Fig. 7-8 presents that the product displays one-dimensional nanostructures which was consisted of a regular quantity of nanofibers. The plain nanofibers formed a web-like appearance and having a uniform diameter with an average of about 150 nm.

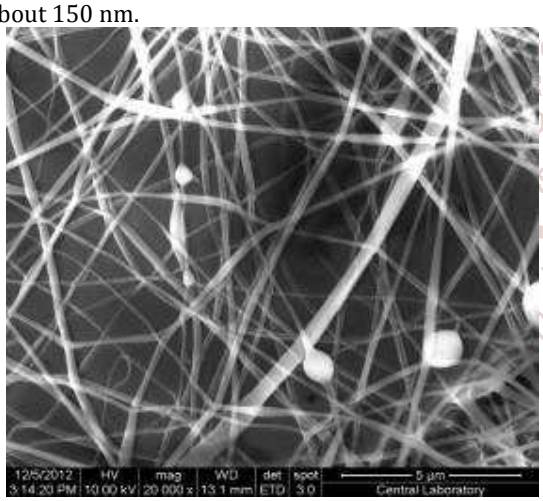

Fig.6. SEM image of synthesized nanofibers before calcined

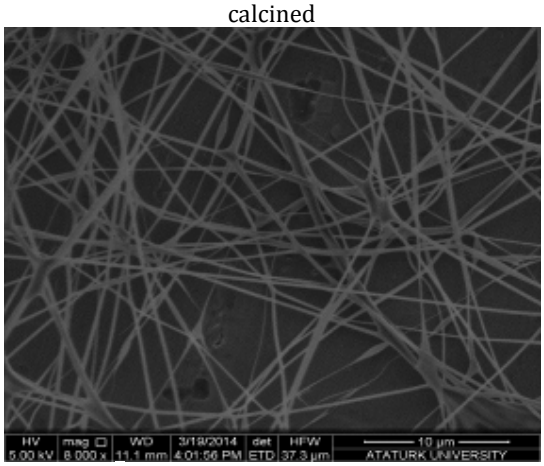

Fig.7. 800 °C SEM image of synthesized nanofibers

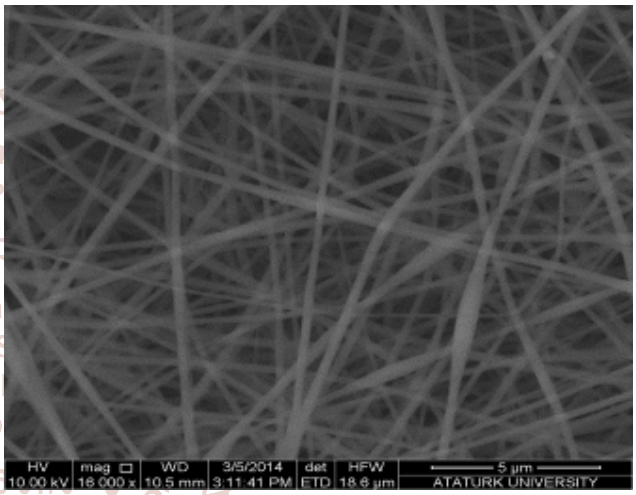

Fig.8. 1200 °C SEM image of synthesized nanofibers

4. CONCLUSIONS

$Mg_2B_2O_5$/PVA fibers were prepared by the sol-gel process and fabricated by electrospinning. This method is simple and effective to produce nanofibers of inorganic oxide composite. On the basis of XRD results of products at different stages, indicate that the formation of $Mg_2B_2O_5$ nanofibers. The SEM investigation unclosed that the diameters of these nanofibers became more uniform after calcination. The TGA thermograms indicated that the thermal stability of the nanofibers was improved, which demonstrated the formation of secondary bonds. In addition, the NMR thermograms at 800-1650 cm^{-1} appears new peak groups, which may be associated to the formation of inorganic phase crystalline at these temperatures. The best yield and the uniform morphology of $Mg_2B_2O_5$ nanofibers can be obtained from high temperature calcination at 800 °C and 1200 °C with diameters down to 100-200 nm.

References

[1] L. Kumari, W. Z. Li, S. Kulkarni, K. H. Wu, W. Chen, C. L. Wang, C. H. Vannoy, R. M. Leblanc, Effect of Surfactants on the Structure and Morphology of Magnesium Borate Hydroxide Nanowhiskers Synthesized by Hydrothermal Route. Nanoscale Research Letters, 5 (2010) 149-157.

[2] W. C. Zhu, G. D. Li, Q. Zhang, L. Xiang, S. L. 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, 203 (2010) 265-271.

[3] S. Li, D. P. Xu, H. Z. Shen, J. Zhou, Y. Fan, Synthesis and Raman properties of magnesium borate micro/nanorods. Materials Research Bulletin, 47 (2012) 3650-3653.

[4] X. Y. Tao, X. D. Li, Catalyst-free synthesis, structural, and mechanical characterization of twinned $Mg_2B_2O_5$ nanowires. Nano Letters, 8 (2008) 505-510.

[5] U. Dosler, M. M. Krzmanc, D. Suvorov, The synthesis and microwave dielectric properties of $Mg_3B_2O_6$ and $Mg_2B_2O_5$ ceramics. Journal of the European Ceramic Society, 30 (2010) 413-418.

[6] Z. S. Hu, R. Lai, F. Lou, L. G. Wang, Z. L. Chen, G. X. Chen, J. X. Dong, Preparation and tribological properties of nanometer magnesium borate as lubricating oil additive. Wear, 252 (2002) 370-374.

[7] M. Koruk, I. Girgin, Synthesis of magnesium borates using sodium borate and magnesium sulfate. Journal of Non-Crystalline Solids, 355 (2009) 965-969.

[8] Y. Zeng, H. B. Yang, W. Y. Fu, L Qiao, L. X. Chang, J. J. Chen, H. Y. Zhu, M. H. Li, GT Zou, Synthesis of magnesium borate ($Mg_2B_2O_5$) nanowires, growth mechanism and their lubricating properties. Materials Research Bulletin, 43 (2008) 2239-2247.

[9] Z. H. Liang, S. Li, P. Z. Lu, C. M. Fan, Electrochemical synthesis of magnesium borate whisker. Journal of Applied Electrochemistry, 41 (2011) 961-963.

[10] A. F. Qasrawi, T. S. Kayed, A.Mergen, M. Gürü, Synthesis and characterization of $Mg_2B_2O_5$. Materials Research Bulletin, 40 (2005) 583-589.

[11] S. H. Chen, P. P. Jin, G. Schumacher, N. Wanderka, Microstructure and interface characterization of a cast $Mg_2B_2O_5$ whisker reinforced AZ91D magnesium alloy composite. Composites Science and Technology 70 (2010) 123-129.

[12] E. M. Elssfah, A. Elsanousi, J. Zhang, H. S. Song, C. Tang: Synthesis of magnesium borate nanorods. Materials Letters 61 (2007) 4358-4361.

[13] W. C. Zhu, L. Xiang, Q. Zhang, X. Y. Zhang, LH u, S.L. Zhu, Morphology preservation and crystallinity improvement in the thermal conversion of the hydrothermal synthesized $MgBO_2(OH)$ nanowhiskers to $Mg_2B_2O_5$ nanowhiskers. Journal of Crystal Growth 310 (2008) 4262-4267.

[14] Y. Z. Jia, S. Y. Gao, S. P. Xia, J. Li, FT-IR spectroscopy of supersaturated aqueous solutions of magnesium borate. Spectrochimica Acta Part a-Molecular and Biomolecular Spectroscopy, 56 (2000) 1291-1297.

[15] S. Li, X. Fang, J. Leng, H. Z. Shen, Y. Fan, D. P. Xu: A new route for the synthesis of $Mg_2B_2O_5$ nanorods by mechano-chemical and sintering process. Materials Letters, 64 (2010) 151-153.

[16] A.S. Kipcak, M. Yildirim, S. Aydin Yuksel, E. Moroydor Derun, S. Piskin, Thesynthesis and physical properties of magnesium borate mineral of admontite synthesized from sodium borates, Adv. Mater. Sci. Eng. 2014 (2014) 1–9.

[17] D.H. Reneker, A.L. Yarin, H. Fong, S. Koombhongse, Bending instability of elec-trically charged liquid jets of polymer solutions in electrospinning, J. Appl. Phys., 87 (2000) 4531.

[18] X. Shi, W. Zhou, D. Ma, Q. Ma, D. Bridges, Y. Ma, et al., Electrospinning of nanofibers and their applications for energy devices, J. Nanomater. 4 (2015) 1–20.

[19] F. Sevim, E. Sevimli, Structure Investigations of $NiO/Al_2O_3/B_2O_3/SiO_2$ Composite Based on PVA Using Sol-Gel Processing and the Electrospinning Technique. Asian Journal of Chemistry, 26 (2014) 2293-2295.

[20] A. L. Yarin, S. Koombhongse, D. H. Reneker, Taylor cone and jetting from liquid droplets in electrospinning of nanofibers, J. Appl. Phys. 90 (2001) 4836.

[21] E. Storti, M. Roso, M. Modesti, C. G. Aneziris, P. Colombo, Preparation and morphology of magnesium borate fibers via electrospinning. Journal of the European Ceramic Society, 36 (2016) 2593-2599.

[22] J. Zhang, Z. Li, B. Zhang, Formation and structure of single crystalline magnesiumborate ($Mg_3B_2O_6$) nanobelts, Mater. Chem. Phys., 98 (2006) 195–197.

[23] F. Sevim, E. Sevimli, F. Demir, T. Çalban, The Effect of Parameters on Productions of $NiO/Al_2O_3/B_2O_3/SiO_2$ Composite Nanofibers by Using Sol-Gel Processing and Electrospinning. World Academy of Science, Engineering and Technology, International Journal of Environmental, Chemical, Ecological, Geological and Geophysical Engineering, 9 (2015) 381-384.