

Pioneer Synthesis and Characterization of Boron Containing Hard Materials

G. Çelik Gül, F. Kurtuluş

Abstract—The first laboratory synthesis of hard materials such as diamond proceeded to attack of developing materials with high hardness to compete diamond. Boron rich solids are good candidates owing to their short interatomic bond lengths and strong covalent character.

Boron containing hard material was synthesized by modified-microwave method under nitrogen atmosphere by using a fuel (glycine or urea), amorphous boron and/or boric acid in appropriate molar ratio. Characterizations were done by x-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy/energy dispersive analyze (SEM/EDS), thermo gravimetric/differential thermal analysis (TG/DTA).

Keywords—Boron containing materials, hard materials, microwave synthesis, powder X-ray diffraction.

I. INTRODUCTION

SUPERHARD materials, generally consisting light elements e.g. boron, carbon, nitrogen, and oxygen, are usually used in manufacturing of cutting tools, scratch-resistant coatings, and abrasives [1]–[6]. The directional bonds of these light elements allow building three-dimensional networks, which is invulnerable to external effects [7]. In general, hardness of the material depends on the temperature and various types of defect. However, most people agree that the hardest material is the highest bulk moduli [8]. Looking from this point of view, these materials can be divided into two subgroups. The first group is diamond-like material adopted tetrahedral arrangement [9], [10]. The second is built by rigid three-dimensional network of icosahedral boron [11].

Hardness is described using Vickers hardness (H_V), meanwhile superhard materials are harder than 40 GPa considering Vickers hardness [12]. In this context, diamond (70-100 GPa) and cubic boron nitride (45-50 GPa) can be accept as superhard materials in industry [12]. Although of all the positive sides, diamond cannot be used to cut steel and ferrous metals resulting iron carbide which is harmful for the human and nature [13], [14]. Cubic boron carbide can be used to cut steel; however, it must be synthesized at high pressure and temperature [14].

The boron suboxide (B_6O) is the richest boron containing material and built of eight icosahedra at the apexes of the rhombohedral unit cell [5], [15]. Two oxygen atoms are located in the interstices along the [111] rhombohedral direction [16]. B_6O has short interatomic bond lengths and

strong covalent character which causes outstanding physical and chemical properties such as low mass density, great hardness, high chemical inertness, and thermal conductivity [17]–[20]. The boron suboxide is a good candidate to apply industry instead of diamond and cubic boron nitride [15]. Boron suboxide was synthesized many times at the temperature range 1800-2100 °C and for 1–24 hours [7], [21]–[29]. Previous studies for obtaining of B_6O are related to conventional synthesized route, which is harmful, time and energy consuming above all costly for the industrial applications.

After the first laboratory synthesis of diamond in 1954, scientists have encouraged to synthesize diamond-like materials which have better designed and improved properties than diamond [30]–[32]. In this context, boron-rich solids started to provide good candidates instead of diamond because of introduction of boron to inorganic synthesis world [33]–[35].

Breathtaking side of this pioneer study is new convenient, low-cost, practical are endless properties of synthesis method to get B_6O with maximum boron contain and apply to every area of the industry easily.

II. EXPERIMENTAL DETAILS

The reactants were supplied by Merck Company as analytically pure. Amorphous boron and glycine were measured 16:1 molar ratio, than they grounded in an agate mortar and put into a porcelain crucible. The mixture was exposed to microwave irradiation under pure nitrogen atmosphere for 30 minutes. The close system described in Fig. 1 was designed by our research group. The pictures were painted by 3D CAD Design Software SOLIDWORKS. The system was drawn same as original structure, and in Fig. 2 the pictures of the system was displayed. The aim of designing of our glass system is to obtain the highest boron containing boroxide by microwave method removing the oxygen from the oven's medium. Thus, we can get both maximum boron containing material and inert atmosphere in same place. The glass part of the system was made by boroglass, connection tubing was made by copper, and plastic pipes. Microwave oven is a kind of domestic oven. Airtightness provided by alumina tape. Ultra-pure nitrogen was used to remove the oxygen from the medium. A gas trap was attached the endpoint to get rid of medium air. A tray filled with silica sand was absorbed the excessive microwave irradiation to prevent the damage to human.

The sample was characterized by X-ray powder diffraction (XRD) pattern using Panalytical X'Pert Pro Diffractometer

and Cu K α radiation ($\lambda=1.54056\text{\AA}$, 40 mA, 50kV). Fourier transform infrared spectra were recorded between 4000 and 600 cm^{-1} using Perkin Elmer Spectrum 100 FTIR Spectrometer. Morphological properties of the sample were realized by ZEISS Supra 40 VP. Thermo gravimetric-differential thermal analysis (TG/DTA) was carried out in a Perkin Elmer Diamond TG/DTA. Siemens V12 domestic microwave oven was used. Ultra-pure nitrogen gas was applied.

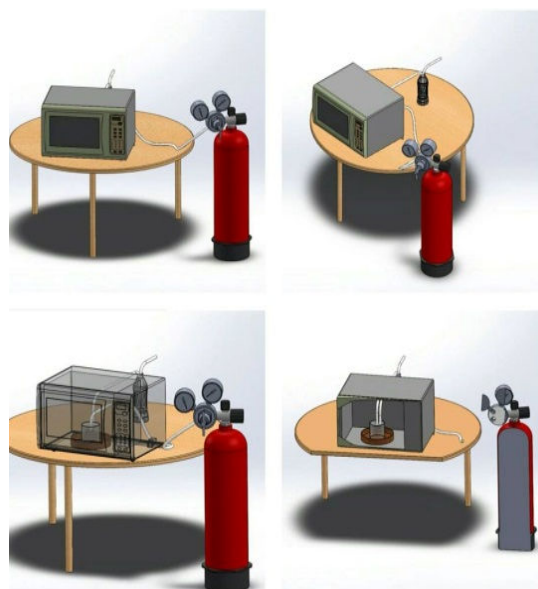


Fig. 1 Personally designed closed glass system



Fig. 2 Pictures of the closed glass system

III. RESULTS AND DISCUSSION

The XRD pattern of the sample was given in Fig. 3. When we compare the pattern to databank, the patterns correspond to B $_6$ O (ICDD = 87-1143). Boron suboxide is crystallized in rhombohedral system with unit cell parameters $a = 5.367$, $c = 12.325$ \AA , and space group R3 m(166). As we saw there is not very clear crystallization on the pattern. But, the main diffractions of the B $_6$ O are present. The basic miller planes

were marked in the figure. We have done FTIR and SEM/EDS analysis to support the formation of the structure. Also, thermal properties of the hard material were discussed.

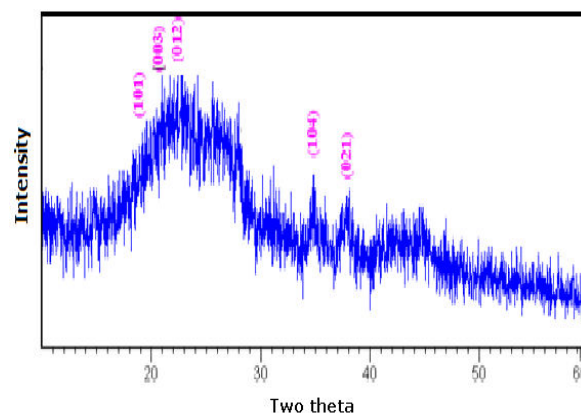


Fig. 3 The XRD pattern of the sample

In Fig. 4, the FTIR spectrum of the sample was given. The wave numbers at 1375, 883, 706, and 633 cm^{-1} are corresponded to various vibrations of BO $_3$ and BO $_4$ groups [36]–[52].

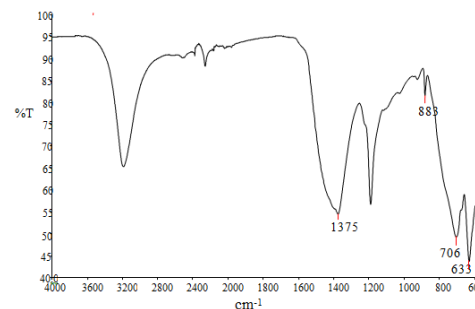


Fig. 4 The FTIR spectrum of the sample

The SEM micrograph was shown in Fig. 5. There is not very homogeneous dispersion because of the incomplete crystallization.



Fig. 5 The morphology of the sample

The EDS analysis of the sample was displayed in Fig. 6. The colors pink and green are corresponded to oxygen and boron, respectively. In the result of EDX, there is no sign of C, H, and N elements of glycine. Probably, the elements vaporized as oxide compounds by the microwave irradiation.

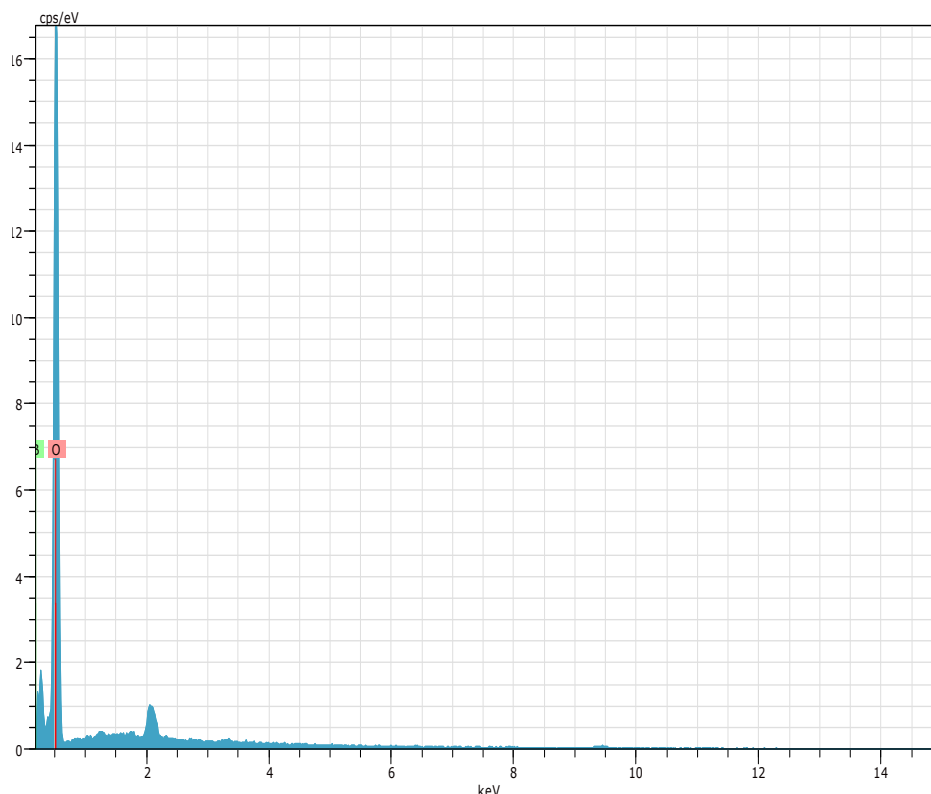


Fig. 6 The EDS results of the sample

In Fig. 7, the TG/DTA curves of the sample were exhibited. The mass loss in the range of 100-200 °C can belong to the surface water and unreacted residues. There is no mass loss in the left range 200-1200 °C means the sample is so stable to the heat treatment.

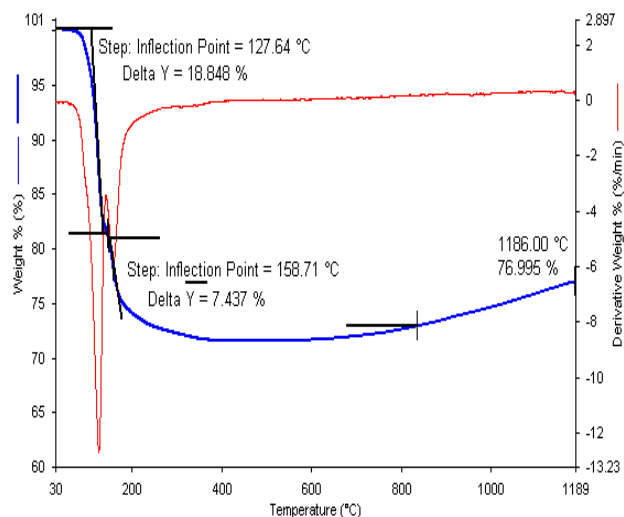


Fig. 7 The thermal behaviour of the sample

IV. CONCLUSION

Briefly, boron is an element promising a bright future due to its short interatomic bonds lengths and strong covalent character in most compounds. The highest boron-containing compound is boron suboxide, which is more than a candidate

to apply industry for cutting tools and coatings. Our closed glass system including nitrogen atmosphere was designed to be practical, low-cost, environmentally friendly, and beyond all applicable to the industry. Boron suboxide exhibits amorphous character was synthesized for the first time via personally designed closed boroglass system as far as is known.

ACKNOWLEDGMENT

We thank to TUBITAK-BIDEB and BAU-Scientific Research Project Unit for their supports.

REFERENCES

- [1] H. Sun, S. Jhi, D. Roundy, M. L. Cohen, and S. G. Louie, "Structural Forms of Cubic BC_2N ," *Phys. Rev. B*, vol. 64, no. 9, pp. 094108, Sep. 2001.
- [2] H. T. Hall, and L. A. Compton, "Group IV Analogs and High-Pressure, High Temperature Synthesis of B_2O_3 ," *Inorg. Chem.*, vol. 4, pp. 1213–1216, Oct. 1965.
- [3] R. H. Wentorf, R. C. DeVries, and F.P. Bundy, "Sintered Superhard Materials," *Science*, vol. 208, no. 4446, pp. 873–880, May 1980.
- [4] A. Y. Liu, and M. L. Cohen, "Prediction of New Low Compressibility Solids," *Science*, vol. 245, no. 4920, pp. 841–842, Aug. 1989.
- [5] H. Hubert, B. Devouard, L. A. J. Garvie, M. O. Keeffe, P. R. Buesck, W. T. Petuskey *et al.*, "Icosahedral Packing of B_{12} Icosahedra in Boron Suboxide (B_6O)," *Nature*, vol. 391, no. 6665, pp. 376–378, Feb. 1998.
- [6] X. Jiao, H. Jin, F. Liu, Z. Ding, B. Yang, F. Lu *et al.*, "Synthesis of Boron Suboxide (B_6O) with Ball Milled Boron Oxide (B_2O_3) under Lower Pressure and Temperature," *J. Solid State Chem.*, vol. 183, no. 7, pp. 1697–1703, July 2010.
- [7] D. He, Y. Zhao, L. Daemen, J. Qian, and T.D. Shen, "Boron Suboxide: as Hard as Cubic Boron Nitride," *Appl. Phys. Lett.*, vol. 81, no. 4, pp. 643–645, July 2002.

- [8] T. Lundsrom, and Y.G. Andreev, "Superhard Boron-Rich Borides and Studies of the B-C-N System," *Mater. Sci. Eng. A*, vol. 209, no. 1-2, pp. 16-22, May 1996.
- [9] E. Parthe, *Crystal Chemistry of Tetrahedral Structures*. Gordon and Breach, Science Publishers: New York, 1964.
- [10] N. A. Goryanova, *The Chemistry of Diamond Like Semiconductors*. Edited by J. C. Anderson, Chapman and Hall, London, 1965.
- [11] H. T. Hall, and L. A. Compton, "Group IV Analogs and High Pressure, High Temperature Synthesis of B₂O," *Inorg. Chem.*, vol. 4, pp. 1213-1216, Aug. 1965.
- [12] S. Veprek, A. Zeer, and R. Riedel, *Handbook of Ceramic Hard Materials*. Edited by R. Riedel Wiley, Weinheim, 2000.
- [13] C. M. Sung, and M. Sung, "Carbon Nitride and Other Speculative Superhard Materials," *Mater. Chem. Phys.*, vol. 43, no. 1, pp. 1-18, Jan. 1996.
- [14] P. F. McMillan, "New Materials from High-Pressure Experiments," *Nat. Mater.*, vol. 1, no. 1, pp. 19-25, Sep. 2002.
- [15] H. Hubert, L. A. J. Garvie, B. Devouard, P. R. Buseck, W. T. Petuskey, and P. F. McMillan, "High-Pressure, High-Temperature Synthesis and Characterization of Boron Suboxide (B₂O)," *Chem. Mater.*, vol. 10, no. 6, pp. 1530-1537, June 1998.
- [16] M. Kobayashi, I. Higashi, C. Brodhag, and F. Thevenot, "Crystal Structure of B₂O," *J. Mater. Sci.*, vol. 28, no. 8 pp. 2129-2134, June 1993.
- [17] S. Lee, S. W. Kim, D. M. Bylander, and L. Kleinman, "Crystal Structure, Formation Enthalpy, and Energy Bands of B₂O," *Phys. Rev. B*, vol. 44, no. 8, pp. 3550-3554, Aug. 1991.
- [18] H. F. Rizzo, W. C. Simmons, and H. O. Bielsstein, "The Existence and Formation of the Solid B₂O," *J. Electrochem. Soc.*, vol. 109, no. 11, pp. 1079-1082, 1962.
- [19] C. E. Hayashi, G. T. Emond, S. Y. Kuo, "Abrasiom of Surfaces with Boron Suboxide, U.S. Patent 920357, 1994.
- [20] T. Lundstrom, "Structure and Bulk Modulus of High-Strength Boron Compounds," *J. Solid State Chem.*, vol. 133, no. 1, pp. 88-92, Oct. 1997.
- [21] D. He, M. Akaishi, B. L. Scott, and Y. Zhao, "Growth of Boron Suboxide Crystals in the B-B₂O₃ System at High Pressure and High Temperature," *J. Mater. Res. Vol.* 17, no. 2, 284-290, Feb. 2002.
- [22] X. Liu, X. Zhao, W. Hou, W. Su, "A New Route for the Synthesis of Boron Suboxide B₂O," *J. Alloys Comp.*, vol. 223, no. 1, pp. L7-L9, May 1995.
- [23] A. R. Barzidan, "Cubic Boron Nitride - Diamond Mixed Crystals," *Mater. Res. Bull.* vol. 16, no.11, pp.1385-1393, Nov. 1981.
- [24] S. Nakano, M. Akaishi, T. Sasaki, and S. Yamaoka, "Segregative Crystallization of Several Diamond-Like Phases from the Graphitic BC₂N without an Additive at 7.7 GPa," *Chem. Mater.*, vol. 6, no. 12, pp. 2246-2251, Dec. 1994.
- [25] E. Knittle, R. B. Kaner, R. Jeanloz, and M. L. Cohen, "High-Pressure Synthesis, Characterization, and Equation of State of Cubic C-BN Solid Solutions," *Phys. Rev. B*, vol. 51, no. 18, pp. 12149-12156, May 1995.
- [26] T. Komatsu, M. Nomura, Y. Kakudate, and S. Fujiwara, "Synthesis and Characterization of a Shock-Synthesized Cubic B-C-N Solid Solution of Composition BC_{2.5}N," *J. Mater. Chem.*, vol. 6, pp. 1799-1803, 1996.
- [27] V. L. Solozhenko, D. Andrault, G. Fiquet, M. Mezouar, and D. C. Rubie, "Synthesis of Superhard Cubic BC₂N," *Appl. Phys. Lett.*, vol. 78, pp. 1385-1387, Nov. 2000.
- [28] V. Srikanth, R. Roy, E. K. Graham, and D. E. Voigt, "B₂O: Phases Present at High Pressure and Temperature," *J. Am. Ceram. Soc.*, vol. 74, no. 12, pp. 3145-3147, Mar. 2005.
- [29] M. Olofsson, and T. Lundstrom, "Synthesis and Structure of Non-Stoichiometric B₂O," *J. Alloys Compd.*, vol. 257, no. 1-2, pp. 91-95, July 1997.
- [30] H. Itoh, I. Maekawa, and H. Iwahara, "High Pressure Sintering of B₂O Powder and Properties of Sintered Compact," *J. Soc. Mater. Sci. Jpn.*, vol. 47, no. 10, pp. 1000-1005, Oct. 1998.
- [31] H. Itoh, R. Yamamoto, and H. Iwahara, "B₂O-c-BN Composites Prepared by High-Pressure Sintering," *J. Am. Ceram. Soc.*, vol. 83, no. 3, pp. 501-506, Mar. 2000.
- [32] T. Taniguchi, M. Akaishi, and S. Yamaoka, "Sintering of Cubic Boron Nitride without Additives at 7.7 GPa and above 2000 °C," *J. Mater. Res.*, vol. 14, no. 1, pp. 162-169, Jan. 1999.
- [33] H. Saitoh, K. Yoshida, and W. Yarbrough, "Crystal Structure of New Composition Boron-Rich Boron Nitride using Raman Spectroscopy," *J. Mater. Res.*, vol. 8, no. 1, pp. 8-11, Dec. 1993.
- [34] D. M. Teter, and R. J. Hemley, "Low-Compressibility Carbon Nitrides," *Science*, vol. 271. no. 1 ,pp. 53-55, Jan. 1996.
- [35] J. Haines, J. M. Leger, and G. Bocquillon, "Synthesis and Design of Superhard Materials," *Annu. Rev. Mater. Sci.*, vol. 31, no. 1, pp. 1-23, Aug. 2001.
- [36] H. Huppertz, S. Altmannshofer, and G. Heymann, "High-Pressure Preparation, Crystal Structure, and Properties of the New Rare-Earth Oxoborate β-Dy₂B₄O₉," *J. Solid State Chem.*, vol. 170, no. 2, pp. 320-329, Feb. 2003.
- [37] F. D. Kurtulus, "Synthesis and Characterization of Metal Containing Borate, Phosphate and Borophosphate Compounds by Hydrothermal and Microwave Methods," PhD thesis, 2003, Balikesir University, Turkey.
- [38] G. Güzel, "Synthesis of Some Type of Lithium and Boron Rich Chemical Compounds and Analyzed Theirs Structural Properties by XRD," MSc. thesis, 2006, Balikesir University, Turkey.
- [39] G. Zhang, Y. Wu, P. Fu, G. Wang, H. Liu, G. Fan, and C. Chen, "A New Sodium Samarium Borate Na₃Sm₂(BO₃)₃," *J. Phys. Chem. Solid*, vol. 63, no. 1, pp. 145-149, Jan. 2002.
- [40] S. Lemanceau, G. C. Bertrand, R. Mahiou, M. El-Ghozzi, J. C. Cousseins, P. Conflnt, and R. N. Vannier, "Synthesis and Characterization of H-LnBO₃ orthoborates (Ln=La, Nd, Sm, and Eu)," *J. Solid State Chem.*, vol. 148, no. 2, pp. 229-235, Dec. 1999.
- [41] B. Tekin, "Syntheses and Structural Characterization of Certain Compound of Metal Borates, Phosphates and Borophosphates," PhD thesis, 2007, Balikesir University, Turkey.
- [42] Y. Shi, J. Liang, H. Zhang, J. Yang, W. Zhuang, and G. Rao, "X-Ray Powder Diffraction and Vibrational Spectra Studies of Rare Earth Borophosphates, Ln₂O₆(BO₃)(PO₃)₂ (Ln=La, Nd, Gd, and Dy)," *J. Solid State Chem.*, vol. 129, no. 1, pp. 45-52, Feb. 1997.
- [43] M. Yerli, "The Synthesis and Characterization of Some Metal Containing Borate, Phosphate and Vanadate Compounds," MSc. thesis, 2009, Balikesir University, Turkey.
- [44] S. Sarıkaya Gacanoğlu, "The Solid State Chemical Synthesis and Characterization Studies of Some New Type Double Metal Orthoborate Compounds," PhD thesis, 2009, Balikesir University, Turkey.
- [45] Y. Zhang, X. L. Chen, J. K. Liang, and T. Xu, "Synthesis and Structural Study of New Rare Earth Sodium Borates Na₃Ln(BO₃)₂ (Ln=Y, Gd)," *J. Alloys and Comp.*, vol. 333, no. 1-2, pp. 72-75, Feb. 2002.
- [46] M. Taşdemir, "Some Theoretical Applications of Rietveld Analysis via GSAS Computer Program on Powder Crystal Systems," MSc. Thesis, 2008, Balikesir University, Turkey.
- [47] G. Gözel, A. Baykal, M. Kızılyalli, and R. Kniep, "Optimizing the Dispersion on an Alumina Suspension Using Commercial Polyvalent Electrolyte Dispersants," *J. Europ. Ceram. Soc.*, vol. 18, no. 14, pp. 2241-2247, Dec. 1998.
- [48] G. Çelik, "The Synthesis and Characterizations Some Types of Vanadate, Borate and Phosphate Compounds which Contains Some Single or Double Metal Atoms," MSc. thesis, 2010, Balikesir University, Turkey.
- [49] K. Nakomato, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, A Wiley-Interscience Publication, John Wiley and Sons, 1986.
- [50] Ş. Somunkıranoğlu, "The Synthesis and Characterization of Oxide and Vanadate Types of Compounds Containing Some Double Metals," MSc. Thesis, 2014, Balikesir University, Turkey.
- [51] A. Baykal, M. Kızılyalli, G. Gözel, and R. Kniep, "Synthesis of Strontium Borophosphate, SrBPO₃ by Solid State and Hydrothermal Methods and Characterization," *Crys. Res. Technol.*, vol. 35, no. 3, pp. 247-254, March 2000.
- [52] A. Baykal, and M. Kızılyalli, "X-Ray Powder Diffraction and IR Study of NaMg(H₂O)₂{BP₂O₈}·H₂O and NH₄Mg(H₂O)₂{BP₂O₈}·H₂O," *J. Mater. Science*, vol. 35, no. 18, pp. 4621-4626, Sep. 2000.

Gülsah Celik Gül was born in Balikesir, Turkey on 9th of July in 1986. She graduated from University of Uludağ, Department of Chemistry in 2008. She has a master degree of science in chemistry from Balikesir University. She has been PhD student at Balikesir University since 2010. Her major field is inorganic chemistry.

She works as a Project Expert at Balikesir University since 2013. She was published eleven articles in SCI-expanded journals related with inorganic chemistry and bioinorganic chemistry. Her current and previous research interests are to material science, bioinorganic chemistry, solid-state chemistry, and crystallography and powder X-ray diffraction.

MSc. Çelik Gül is a member of Turkish Chemistry Society and Turkish Biochemical Society.

Figen Kurtulus was born in Balıkesir, Turkey in 1972. She graduated from University of Uludağ Department of Chemistry Education in 1993. She has a master degree of science and PhD in chemistry from Balıkesir University. Her major field is inorganic chemistry.

She has been Assoc. Prof. Dr at Balıkesir University Chemistry Department since 2011. She was published twenty articles in SCI-expanded journals related with inorganic chemistry and solid state chemistry. Her current and previous research interests are to inorganic chemistry, material science, solid-state chemistry, and crystallography and powder X-ray diffraction.

Assoc. Prof. Dr. Kurtuluş is a member of Turkish Chemistry Society.