Research Article

Open Access

Ali Can Ersan, Azmi Seyhun Kipcak, Meral Yildirim Ozen and Nurcan Tugrul*

An accelerated and effective synthesis of zinc borate from zinc sulfate using sonochemistry

<https://doi.org/10.1515/mgmc-2020-0002>

Received November 11, 2019; accepted February 14, 2020.

Abstract: Recently, sonochemistry has been used for the synthesis of inorganic compounds, such as zinc borates. In this study using zinc sulphate heptahydrate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) and boric acid (H_3BO_3) as starting materials, a zinc borate compound in the form of $\text{Zn}_3\text{B}_6\text{O}_{12} \cdot 3.5\text{H}_2\text{O}$ was synthesized using an ultrasonic probe. Product's characterization was carried out with using X-ray diffraction (XRD), Scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FT-IR) and Raman spectroscopy. Zinc borate compound's chemical bond structure was observed with Raman and FTIR. From the XRD results it was seen that $\text{Zn}_3\text{B}_6\text{O}_{12} \cdot 3.5\text{H}_2\text{O}$ can be quickly synthesized upon heating at 80°C and 85°C (55 min) or 90°C (45 min) in very high yield (>90%). The minimum particle size obtained was ~143 µm from the SEM results. Zinc borate compound was synthesized at a lower temperature in less time than other synthesized zinc metal compound in literature.

Keywords: ultrasonic irradiation; sonochemistry; zinc borate; reaction yield

1 Introduction

Zinc borate (ZB) compounds are used in a wide range of applications in plastics, ceramics, electrical insulation, wood, wire, cement, pharmaceuticals, paint, and rubber

(Ata et al., 2011; Chen et al., 2009; Gao and Liu., 2009; Gönen et al., 2009; Gürhan et al., 2009; Igarashi et al., 2004; Nies and Campbell, 1980; Schubert et al., 2002; Yumei et al., 2006). Zinc borates can be used as non-flammable and fire retardant additives in PVC, halogenated polyester and nylon, as combustion retardants and corrosive inhibitors, in the manufacture of refractory plastic materials, in electric/electronic materials, in the textile and paper industries and as a fungicide/insecticide in wood accessories (Gürhan et al., 2009; Schubert et al. 2002).

Several studies have been carried out towards the synthesis of zinc borate using a hydrothermal method. Gürhan et al. (2009) carried out 3.5 mol hydrated zinc borate' synthesis and examined synthesis parameters' effects. Nies and Campbell (1980) carried out the synthesis of zinc borate using sodium potassium tetraborate ($\text{K}_2\text{B}_4\text{O}_7$) and zinc chloride, bromide, sulfate and nitrate as the starting materials at 95°C for 5.5, 6 and 24 h., respectively. Yumei et al. (2006) obtained crystal and hydrophobic zinc borate nanodiscs using borax tetraborate decahydrate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) and zinc sulfate heptahydrate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) via a hydrothermal method. Oleic acid was used as a modifying agent. The reaction was realized at 70°C for 6.5 h. Igarashi et al. (2004) have synthesized zinc borate using a two-step reaction. This involved heating boric acid (H_3BO_3) and zinc oxide (ZnO) at 60°C for 1.5 h. to form the initial crystals of zinc borate, which were then further heated at 90°C for 4 h. Gao and Liu (2009) studied the synthesis of zinc borate hydrated minerals under reflux conditions with 11 h. Ata et al. (2011) have studied the synthesis of zinc borates using zinc oxide (ZnO) and boric acid (H_3BO_3) at 68-120°C, a rotating speed of 333-767 rpm over 60-200 min. At the end of their study, the optimum yield was obtained at 85°C, 766 rpm and 183 min with the conversion of zinc oxide found to be 99%. Chen et al. (2009) carried out the synthesis of ZB nano-flakes ($2\text{ZnO} \cdot 2\text{B}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) with the coordination and homogeneous precipitation of ammonia, borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) and zinc nitrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$). Zheng et al. (2009) produced zinc $4\text{ZnO} \cdot \text{B}_2\text{O}_3 \cdot \text{H}_2\text{O}$ that is form of zinc borate using with $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. Acarali et al. (2013) examined different modification agents' effects used

* **Corresponding author: Nurcan Tugrul**, Faculty of Chemical and Metallurgical Engineering, Chemical Engineering, Yildiz Technical University, Davutpasa Campus, Davutpasa Street No. 127, 34210 Esenler, Istanbul, Turkey, e-mail: ntugrul@yildiz.edu.tr, tel: +90-212 3834771, fax: +90-212 3834725

Ali Can Ersan, Azmi Seyhun Kipcak and Meral Yildirim Ozen, Faculty of Chemical and Metallurgical Engineering, Chemical Engineering, Yildiz Technical University, Davutpasa Campus, Davutpasa Street No. 127, 34210 Esenler, Istanbul

to procure hydrophobic zinc borate product at between 50-120°C over 1-5 h. Kipcak et al. (2016) obtained zinc borate from boric acid and zinc oxide 1-5 h and at 95°C.

Sonochemical systems create multi-bubble environments in which chemical reactions occur with the strong and rapid connection of the reactants. In a sonochemical synthesis, the chemical reactions are carried out using the kinetic energy supplied from acoustic cavitation. The acoustic cavitation ensures high pressure, high temperature and high energy levels to the reactants for a very short period of time and accelerates the reactions with high reaction efficiencies (Lupacchini et al., 2017; Mettin et al., 2015; Timothy et al., 2017).

The hydrothermal synthesis of zinc borates has been widely studied and reported in the literature. In our research group, we have studied the ultrasonic synthesis of zinc borates using ZnO and $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ as the starting materials (Ersan et al., 2016). Due to the high cost of the starting materials used these two studies with respect to $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, this study's novelty is the cheap and rapid synthesis's of zinc borate by using the method of sonochemistry.

2 Results and discussion

2.1 The starting materials' XRD results

The starting materials were characterized by XRD analysis. $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ was identified as "goslarit ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$)" with the powder diffraction file (pdf) No. 01-075-0949. $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$ was identified as "tincalconite ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$)" with the pdf No. 00-007-0277. $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ was identified as "borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$)" with the pdf No. 01-075-1078. The commercial zinc borate was defined as "zinc oxide borate hydrate ($\text{Zn}_3\text{B}_6\text{O}_{12} \cdot 3.5\text{H}_2\text{O}$)" with the pdf No. 00-035-0433.

2.2 The as-synthesized zinc borate compounds' XRD results and their reaction yields

According to the XRD results, the as-synthesized compound was defined as "zinc oxide borate hydrate ($\text{Zn}_3\text{B}_6\text{O}_{12} \cdot 3.5\text{H}_2\text{O}$)" with the pdf No. "00-035-0433" and was identical to that previously reported in the literature (Bardakci et al., 2013; Ersan et al., 2016; Kipcak et al., 2014, 2015, 2016; Vardar et al., 2017). The as-synthesized zinc borate compound's XRD results are given in Figure 1.

According to the XRD results, the minimum required reaction time to complete formation of zinc borate was 55 min at 80°C and 85°C and 45 min at 90°C in SET-1; 55 min at 85°C and 45 min at 90°C in SET-2 and 55 min at 80°C, 50 min at 85°C and 45 min at 90°C in SET-3. In SET-1, at 80°C and 50 min the zinc borate was partly synthesized. The lowest XRD score was obtained in SET-1 and the highest XRD score was procured in SET-2. The XRD score is a similarity measure of the as-synthesized compound with the reference pdf card. Meaning that all of the peak intensities (%) and peak locations matched perfectly with the pdf card number of reference mineral, the XRD score of analyzed mineral is equal to 100 (Kipcak et al., 2016).

The compounds' XRD patterns with the highest XRD scores are given in Figure 2. The characteristic peaks are in mutual agreement with the studies reported in the literature (Ersan et al., 2016; Kipcak et al., 2014, 2015, 2016; Vardar et al., 2017). In addition, the as-obtained XRD scores were slightly higher than those previously reported in the literature (Table 1).

The reaction yields are given in Figure 3, which shows that the reaction yields were increased by the increase in reaction time and temperature. In addition, the highest and the lowest reaction yields were obtained in SET-3, and SET-1, respectively. The highest reaction yields were procured at 90°C over 55 min for all of the sets, which were calculated to be $98.3 \pm 0.2\%$, $98.4 \pm 0.2\%$ and $99.2 \pm 0.3\%$ for SET-1, SET-2 and SET-3, respectively. In accordance with the XRD scores, the reaction yields were found to be higher than those previously reported in the literature and significantly higher than those reported by Ersan et al. (2016) and Vardar et al. (2017).

2.3 The as-synthesized zinc borate compounds' FT-IR and Raman spectroscopy

The optimum zinc borate compounds' recorded IR spectra from chosen reactions are given in Figure 4. The range of bands 1412 cm^{-1} and 1253 cm^{-1} are associated with the three-coordinate boron to oxygen bonds' [$\nu_{\text{as}}(\text{B}_{(3)}-\text{O})$] asymmetric stretching. The range of bands 1196 cm^{-1} and 1113 cm^{-1} correspond to the boron-oxygen-hydrogen bonds' bending [$\delta(\text{B}-\text{O}-\text{H})$]. The IR peaks around 1064 cm^{-1} can be attributed to the four-coordinate boron to oxygen bonds' asymmetric stretching [$\nu_{\text{as}}(\text{B}_{(4)}-\text{O})$]. The IR peaks observed at $\sim 930\text{ cm}^{-1}$ are associated with the three-coordinate boron to oxygen bonds' symmetric stretching [$\nu_{\text{s}}(\text{B}_{(3)}-\text{O})$]. The bands between 858 cm^{-1} and 798 cm^{-1} correspond to the four-coordinate boron to oxygen bonds' symmetric

Figure 1: The XRD scores of the as-synthesized zinc borate compounds.

Figure 2: The XRD patterns of the high-scoring zinc borate compounds.

Table 1: The synthesis parameters used to prepare $\text{Zn}_3\text{B}_6\text{O}_{12} \cdot 3.5\text{H}_2\text{O}$ compound previously reported in the literature.

Synthesis method	Starting materials	Reaction Temp. (°C)	Reaction time (min)	XRD Score	Reaction yield (%)	Reference
Hydrothermal	$\text{ZnO-H}_3\text{BO}_3$	95	120	n.a.	86.78	Bardakci et al., 2013
		80	180	70	87.10	Kipcak et al., 2014
		90	180	68	91.80	Kipcak et al., 2014
		100	120	75	95.70	Kipcak et al., 2014
	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O-NaOH-H}_3\text{BO}_3$	70	180	80	88.10	Kipcak et al., 2015
		80	180	81	93.00	Kipcak et al., 2015
		90	120	78	96.10	Kipcak et al., 2015
	$\text{ZnCl}_2\text{-NaOH-H}_3\text{BO}_3$	70	240	70	86.50	Kipcak et al., 2015
		80	120	61	75.50	Kipcak et al., 2015
		90	120	75	97.80	Kipcak et al., 2015
	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O-Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O-H}_3\text{BO}_3$	70	240	69	86.50	Kipcak et al., 2016
		80	240	72	96.50	Kipcak et al., 2016
		90	180	72	99.60	Kipcak et al., 2016
	$\text{ZnCl}_2\text{-Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O-H}_3\text{BO}_3$	70	240	68*	n.a.	Kipcak et al., 2016
		80	120	70	86.20	Kipcak et al., 2016
		90	120	72	87.70	Kipcak et al., 2016
Ultrasonication	$\text{ZnO-H}_3\text{BO}_3$	80	55	64	89.10	Ersan et al., 2016
		85	55	65	92.40	Ersan et al., 2016
		90	50	60	93.20	Ersan et al., 2016
	$\text{Zn}_5(\text{CO}_3)_2 \cdot (\text{OH})_6 \cdot \text{H}_3\text{BO}_3$	80	50	55	90.34	Vardar et al., 2017
		85	40	56	91.38	Vardar et al., 2017
		90	40	58	91.79	Vardar et al., 2017

stretching. $[\nu_s(\text{B}_{(4)}\text{-O})]$. The IR peak at 753 cm^{-1} corresponds to the vibrations which belong to the $[\nu_p(\text{B}(\text{OH})_4)]$ band. The IR peaks observed at $\sim 659\text{ cm}^{-1}$ are attributed to the three-coordinate boron to oxygen bonds' the bending $[\gamma(\text{B}_{(3)}\text{-O})]$. The bands are in mutual agreement with the studies of Ersan et al. (2016), Kipcak et al. (2014, 2015, 2016) and Vardar et al. (2017).

The zinc borate compounds' recorded Raman spectra from chosen reactions are given in Figure 5. The peaks at $\sim 1047\text{ cm}^{-1}$ originate from $\nu_{\text{as}}(\text{B}_{(4)}\text{-O})$ and the $\nu_p(\text{B}(\text{OH})_4)$ scattering was observed at $\sim 755\text{ cm}^{-1}$. The peaks at 664 cm^{-1} correspond to the bending of $\gamma(\text{B}_{(3)}\text{-O})$ and the peaks corresponding to the $(\text{B}_{(3)}\text{-O}) / \delta(\text{B}_{(4)}\text{-O})$ bonds are observed at 579 cm^{-1} . Obtained bands are in mutual agreement with the studies of Ersan et al. (2016), Kipcak et al. (2014, 2015, 2016) and Vardar et al. (2017).

2.4 Synthesized zinc borate compounds

SEM results

SEM images of the selected samples of zinc borate obtained from each reaction set are displayed in Figure 6.

It can be observed that for all the starting materials, the as-obtained zinc borate compounds were agglomerates of sub-microscale elliptic particles. When the morphology of the as-synthesized zinc borate particles was compared with that of a previous study, in which $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ was used as the zinc source, it was observed that the use of an ultrasonic synthesis method changed the shape of the as-obtained particles given in Kipcak et al. (2016). For SET-1, products' particle size was observed to be between 942.52 nm and 179.11 nm . On the other hand, when sodium borate was used as the boron source, products' particle size was reduced to 143.41 nm (SET-2). For SET-3, the particle products' particle size was observed to be between 596.63 nm and 156.03 nm .

3 Conclusion

In this study, zinc borate in the form of $\text{Zn}_3\text{B}_6\text{O}_{12} \cdot 3.5\text{H}_2\text{O}$ was synthesized from various boron sources and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ via a sonochemical synthesis method. Based on the results, the following conclusions can be drawn:

Figure 3: The reaction yields of the as-synthesized zinc borate compounds.

Figure 4: The FT-IR spectra of the selected zinc borate compounds.

- Ultrasonification reduced the synthesis time of zinc borate to 45 min at 90°C and the reaction yield using these synthesis parameters was $98.4 \pm 0.3\%$.
- The spectroscopic results showed that the products had the characteristic band vibrations in both the IR and visible-light regions.
- The SEM images of the zinc borate compounds proved that the synthesis method influenced the particle morphology and size.
- Being an energy saving, rapid and effective method makes this sonochemical synthesis an alternative pathway for the green synthesis of zinc borate.

Figure 5: The Raman spectra of the selected zinc borate compounds.

Figure 6: The SEM morphologies of the selected zinc borate compounds: (a) SET-1, (b) SET-2 and (c) SET-3 (10000× magnification).

Experimental

Reagents

The boron starting materials, H_3BO_3 , $Na_2B_4O_7 \cdot 10H_2O$ and $Na_2B_4O_7 \cdot 5H_2O$, were provided from Bandırma Boron Works (Eti Maden, Balıkesir, Turkey) with a minimum purity of 99.9%. The other starting materials, $ZnSO_4 \cdot 7H_2O$ (purity $\geq 97.0\%$) and NaOH (purity $\geq 99.0\%$) were provided from Merck Chemicals (Merck KGaA, Darmstadt, Germany) and used without any pretreatment. Commercial seed of zinc borate provided from Melos A.Ş. (Melos A.Ş., Istanbul, Turkey) was used in the synthesis. The XRD analysis of starting materials was performed on a PANalytical Xpert Pro (PANalytical B.V., Almelo, The Netherlands) X-ray diffractometer (XRD) using Cu-K α radiation ($\lambda = 1.53 \text{ \AA}$) at 45 kV and 40 mA.

Synthesis of the compounds

Several pre-experiments were performed to obtain the optimum rate of starting materials for zinc borate synthesis. Among these pre-experiments, the optimum ratio of the zinc and boron starting materials was found to be 1:7 in SET-1 and 1:8 in SET-2 and SET-3, respectively. At these ratios, the expected reactions are given by Eq. 1-3:

Table 2: The quantity of starting materials used in the zinc borate syntheses.

SET-1	ZnSO ₄ ·7H ₂ O (mol)	NaOH (mol)	H ₃ BO ₃ (mol)	Zn/B (mol/mol)
	0.018	0.036	0.126	7
SET-2	ZnSO ₄ ·7H ₂ O (mol)	Na ₂ B ₄ O ₇ ·5H ₂ O (mol)	H ₃ BO ₃ (mol)	Zn/B (mol/mol)
	0.018	0.018	0.072	8
SET-3	ZnSO ₄ ·7H ₂ O (mol)	Na ₂ B ₄ O ₇ ·10H ₂ O (mol)	H ₃ BO ₃ (mol)	Zn/B (mol/mol)
	0.018	0.018	0.072	8

For the sonochemical synthesis, a temperature controlled batch type glass reactor (100 mL capacity) equipped with a cooling jacket was used. Pure water obtain from a GFL 2004 instrument (Gesellschaft für Labortechnik, Burgwedel, Germany) was used as the liquid medium. In the synthesis, the appropriate amount of H₃BO₃ was dissolved in 25 mL of pure water and heated to the target temperature. ZnSO₄·7H₂O, NaOH and commercial zinc borate seed (1% w/w as H₃BO₃) were then added for SET-1. Na₂B₄O₇·5H₂O and Na₂B₄O₇·10H₂O were used instead of NaOH for SET-2 and SET-3, respectively. The amounts of the starting materials used are given in Table 2.

A Bandelin Sonopuls HD 2070 (20 kHz) model ultrasonic homogenizer (Bandelin electronic GmbH & Co. KG, Berlin, Germany) was used for the synthesis. After the determined reaction time, the slurry was filtered and washed with purified water (70-80°C) to remove the unreacted H₃BO₃ and Na₂SO₄ from the synthesized zinc borate compound. Then, the resulting solid was dried using an EcoCELL 111 model incubator (MMM Medcenter Einrichtungen GmbH, Planegg, Germany) at 105°C to remove the excess water. The reaction procedure is identical to that reported to Ersan et al. (2016). For examine reaction parameters' effects on the as-synthesized compounds, the synthesis procedure was repeated at 80, 85 and 90°C and with reaction times of 40, 45, 50 and 55 min, respectively.

3.1 Zinc borate compounds' characterization

The as-synthesized zinc borate compounds were characterized by XRD analysis, Raman spectroscopy and FTIR. The crystalline structure of the products was analyzed using XRD. The reaction efficiency calculations were carried out using ZnSO₄·7H₂O as the limiting reactant. The reaction efficiency (Y_D) was calculated using Eq. 4 (Fogler, 1999):

$$Y_D = \frac{N_D}{N_{AO} - N_A} \quad (4)$$

where N_D presents consumed key reactant's number of moles. N_{AO} and N_A present key reactant's the initial and final moles.

The FT-IR spectra were recorded on a PerkinElmer Spectrum One model FT-IR spectrometer (PerkinElmer, MA, USA) equipped with a universal attenuation total reflectance (ATR) sampling accessory in the spectral range between 1800-650 cm⁻¹. The as-synthesized zinc borate samples' Raman spectra were measured on a Perkin Elmer Raman Station 400F (PerkinElmer, CT, USA) Raman spectrometer's range between 1600-250 cm⁻¹. These spectral ranges were selected due to the characteristic vibration range of boron minerals. The morphology and surface properties of the zinc borate particles were observed on a CamScan brand Apollo 300 field-emission SEM (CamScan, Oxford, UK) equipped with a back-scattering electron (BSE) detector at 15 kV. The magnification was set to 10000.

References

- Acarali N.B., Tugrul N., Derun E.M., Piskin S., Production and characterization of hydrophobic zinc borate by using palm oil. *Int. J. Min. Met. Mater.*, 2013, 20, 1081-1088.
- Ata O.N., Sayan E., Engin, B., Optimization and Modeling of Zinc Borate (2ZnO·3B₂O₃·3.5H₂O) Production with the Reaction of Boric Acid and Zinc Oxide. *J. Ind. Eng. Chem.*, 2011, 17, 493-497.
- Bardakci M., Acarali N.B., Tugrul N., Derun E.M., Piskin M.B., Production of Zinc Borate for Pilot-Scale Equipment and Effects of Reaction Conditions on Yield. *Mater. Sci.-Medzg.*, 2013, 19, 158-163.
- Chen T., Deng J.-C., Wang L.-S., Feng G., Preparation and characterization of nano-zinc borate by a new method. *J. Mater. Process. Tech.*, 2009, 209, 4076-4079.
- Ersan A.C., Yildirim M., Kipcak A.S., Tugrul N., A Novel Synthesis of Zinc Borates from a Zinc Oxide Precursor via Ultrasonic Irradiation. *Acta Chim. Slov.*, 2016, 63, 881-890.

- Fogler H.S., Elements of Chemical Reaction Engineering (3rd ed.). Prentice-Hall, Englewood Cliffs, NJ, USA, 1999.
- Gao Y.H., Liu Z., Synthesis of an industrially important zinc borate, $2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, by a rheological phase reaction method. *Thermochim. Acta*, 2009, 484, 27-31.
- Gönen M., Balkose D.R., Gupta B., Ulku S., Supercritical carbon-dioxide drying of methanol zincborate mixtures. *Ind. Eng. Chem. Res.*, 2009, 48, 6869-6876.
- Gürhan D., Çakal G.Ö., Eroğlu İ., Özkar S., Improved Synthesis of Fine Zinc Borate Particles Using Seed Crystals. *J. Cryst. Growth*, 2009, 311, 1545-1552.
- Igarashi H., Sawada H., Tatebe A., Sakao K., Zinc borate and production method and use there of. European Patent Office, Patent No: EP 1 205 439 A, 2004, 1-38.
- Kipcak A.S., Acarali N.B., Derun E.M., Tugrul N., Piskin S., Effect of magnesium borates on the fire-retarding properties of zinc borates. *J. Chem.*, 2014, 512164, 1-12.
- Kipcak A.S., Senberber F.T., Derun E.M., Tugrul N., Piskin S., Characterization and thermal dehydration kinetics of zinc borates synthesized from zinc sulfate and zinc chloride. *Res. Chem. Intermediat.*, 2015, 41, 9129-9143.
- Kipcak A.S., Senberber F.T., Yildirim M., Yuksel S.A., Derun E.M., Tugrul N., Characterization and physical properties of hydrated zinc borates synthesized from sodium borates. *Main Group Met. Chem.*, 2016, 39, 59-66.
- Lupacchini M., Mascitti A., Giachi G., Tonucci L., d'Alessandro N., Martinez J., et al., Sonochemistry in non-conventional, green solvents or solvent-free reactions. *Tetrahedron*, 2017, 73, 609-653.
- Mettin R., Cairós C., Troia A., Sonochemistry and bubble dynamics. *Ultrason. Sonochem.*, 2015, 25, 24-30.
- Nies N.P., Campbell N.P.G.W., *Inorganic and Theoretical Chemistry*. Longman, London, United Kingdom, 1980, 53-231.
- Schubert D., Alam F., Visi M., Knobler C., Structural Characterization and Chemistry of the Industrially Important Zinc Borate, $\text{Zn}[\text{B}_3\text{O}_4(\text{OH})_3]$. *Chem. Mat.*, 2002, 15, 866-871.
- Timothy J.M., Sonochemistry and sonoprocessing: the link, the trends and (probably) the future. *Ultrason. Sonochem.*, 2017, 10, 175-179.
- Vardar D.S., Senberber F.T., Kıpçak A.S., Tuğrul N., A green sonochemical synthesis of zinc borates from $\text{Zn}_5(\text{CO}_3)_2 \cdot (\text{OH})_6$. *Main Group Chem.*, 2017, 16, 160-170.
- Yumei T., Yupeng G., Jiang M., Sheng Y., Bala H., Zhang G., et al., Synthesis of hydrophobic zinc borate nanodiscs for lubrication. *Mater. Lett.*, 2006, 60, 2511-2515.
- Zheng Y., Tian Y., Ma H., Qu Y., Wang Z., An D., et al., Synthesis and Performance Study of Zinc Borate Nanowhiskers. *Colloid. Surface. A*, 2009, 339, 178-184.