The Determination of the Zinc Sulfate, Sodium Hydroxide and Boric Acid Molar Ratio on the Production of Zinc Borates

N. Tugrul, A. S. Kipcak, E. Moroydor Derun, S. Piskin

***Abstract*—**Zinc borate is an important boron compound that can be used as multi-functional flame retardant additive due to its high dehydration temperature property. In this study, the raw materials of $ZnSO_4.7H_2O$, NaOH and H_3BO_3 were characterized by X-Ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FT-IR) and used in the synthesis of zinc borates. The synthesis parameters were set to 100°C reaction temperature and 120 minutes of reaction time, with different molar ratio of starting materials ($ZnSO_4.7H_2O$:NaOH:H_3BO_3). After the zinc borate synthesis, the identifications of the products were conducted by XRD and FT-IR. As a result, Zinc Oxide Borate Hydrate [$Zn_3B_6O_{12}.3.5H_2O$], were synthesized at the molar ratios of 1:1:3, 1:1:4, 1:2:5 and 1:2:6. Among these ratios 1:2:6 had the best results.

***Keywords*—**Zinc borate, $ZnSO_4.7H_2O$, NaOH, H_3BO_3, XRD, FT-IR.

I. Introduction

ZINC borate have many application areas ranging from polymers to paints. Different types of zinc borates that are important inorganic hydrated borates can be used as flame and fire retardant and corrosion inhibitor [1], [2]. Depending the contents of zinc and boric oxides, its properties varies and used widely in plastic, rubber, ceramics, paint, wire, electrical insulation, wood applications, cement and pharmaceutical industries [3], [4]. Also zinc borates can be grouped in the synthetic hydrate metal borates [5].

Zinc borate is produced by reaction between aqueous boric acid and zinc oxide above 70°C. Zinc borate is ($2ZnO.3B_2O_3.3.5H_2O$) one of the several types of zinc borates. This compound has the unusual property of retaining its water of hydration at temperatures up to 290°C. This thermal stability makes it attractive as a fire retardant additive for plastics and rubbers that require high processing temperatures. It is also used as an anticorrosive pigment in coatings [6].

The preparation of $2ZnO{\cdot}3B_2O_3{\cdot}3H_2O$ from zinc oxide and boric acid by a rheological phase reaction is studied by Shi et al. [7]. XRD, TG, DTA and SEM used for the characterization analyses. In addition, the effects of experimental conditions and particle size distribution on the characteristics of the products were studied. The synthetic method for the production of zinc borates is easy, pollution friendly and have high reaction yield between 95-99%. Additionally, zinc borate it can be used to remove various toxic gases and organic compounds.

Igarashi et al. [8] studied the synthesis of zinc borates in a two-step reaction. First step, zinc oxide and boric acid were combined and stirred at 60°C for 1.5 hours to achieve crystal formation. In the second step, the mixture was stirred continuously at 90°C for 4 hours, and seed crystals were added to the reaction mixture to enhance crystal growth.

In this study, the determination of the optimum molar ratio of zinc sulfateheptahydrate ($ZnSO_4.7H_2O$), sodium hydroxide (NaOH) and boric acid (H_3BO_3) is aimed in the hydrothermal synthesis of zinc borates. Synthesized products are characterized by Philips Panalytical, Xpert-ProX-Ray Diffraction (XRD) and Perkin Elmer, Spectrum One Fourier Transform Infrared Spectroscopy (FT-IR).

II. Materials and Methods

A. Raw Materials

$ZnSO_4.7H_2O$ was supplied from Sigma Aldrich Reagent Plus® (≥99.0%purity), NaOH was supplied from Merck Chemicals (Product number: 1.06462.5000, ≥ 97.0% purity) and H_3BO_3wasretrieved from Kirka Boron Management Plant in Bandirma. $ZnSO_4.7H_2O$ and NaOH were used without pretreatment and H_3BO_3 was treated using agate mortar and sieved to 200 meshes (Fig. 1). Characterizations of $ZnSO_4.7H_2O$ and H_3BO_3wereconducted by XRD (Fig. 2) and FT-IR spectroscopy with Universal ATR sampling accessory – Diamond / ZnSe Crystal (Fig. 3).

Fig. 1 (a) Agate mortar, (b) Sieve

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Fig. 2 Philips PANalytical XRD

Fig. 3 Perkin Elmer Spectrum One FT-IR Spectrometer

B. Hydrothermal Syntheses and Characterizations

In the synthesis, several molar ratios of the $ZnSO_4.7H_2O$ (Z) NaOH (N) and H_3BO_3(H) were tested. Demineralized water (18.3 mΩ.cm) that produced from the equipment of Human Power I+ Water Purification System was used at the liquid phase.

Experiment temperature was selected as 100°C, and reaction time were set to 120 minutes. These parameters were selected from the study of Tugrul et al. [9].

H_3BO_3wasdissolved in demineralized water at the 100°C temperature then $ZnSO_4.7H_2O$ and NaOH were added. After the addition of NaOH, commercial zinc borate ($Zn_3B_6O_{12}.3.5H_2O$) retrieved from local market in Turkey (in terms of H_3BO_3, 0.5% w/w) was added. At the end of the 120 minutes, formed zinc borate crystals were washed with distilled water and dried in the oven at 105°C for 24 hours. Obtained products were characterized by XRD and FT-IR.

III. Results and Discussion

A. Raw Material Characterization

XRD patterns and results of $ZnSO_4.7H_2O$, H_3BO_3 and commercial $Zn_3B_6O_{12}.3.5H_2O$ were given in Figs. 4-6 and Table I.

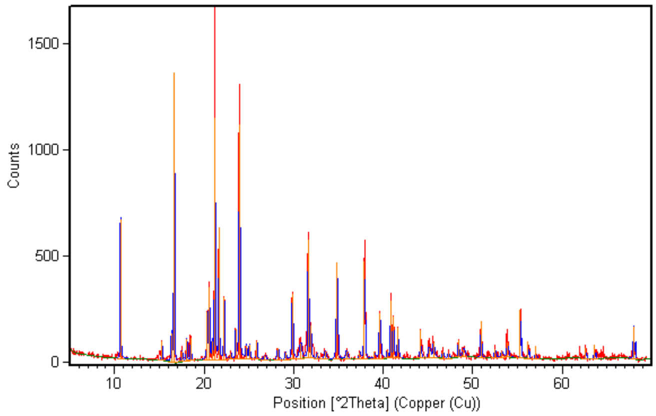

Fig. 4 XRD pattern of $ZnSO_4.7H_2O$

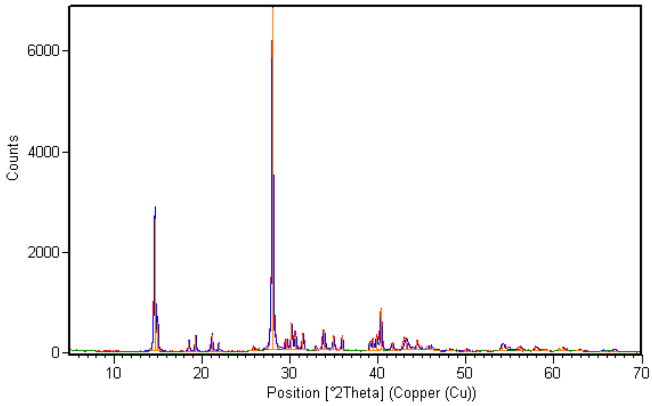

Fig. 5 XRD pattern of H_3BO_3

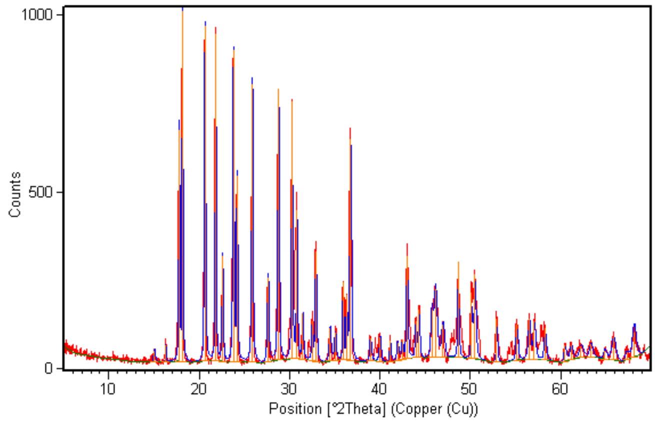

Fig. 6 XRD pattern of commercial $Zn_3B_6O_{12}.3.5H_2O$

TABLE I
XRD Results of Raw Materials

Reference Code	Compound Name	Chemical Formula	Score
01-075-0949	Bianchite	ZnSO4.6H_2O	55
00-009-0395	Goslarite	ZnSO4.7H_2O	24
01-073-2158	Sassolite	H_3BO_3	62
00-035-0433	Zinc Oxide Borate Hydrate	$Zn_3B_6O_{12}.3.5H_2O$	80

From the XRD analysis of $ZnSO_4.7H_2O$, it is seen that compound was consist of “01-075-0949” coded bianchite and

"00-009-0395" coded goslarite, that their structural formulas are $ZnSO4.6H_2O$ and $ZnSO4.7H_2O$, respectively. H_3BO_3 and commercial $Zn_3B_6O_{12}.3.5H_2O$ were found as, "01-073-2158" coded sassolite (H_3BO_3) and "00-035-0433" coded zinc oxide borate hydrate, respectively.

FT-IR spectrum of $ZnSO_4.7H_2O$, NaOH,H_3BO_3 and commercial $Zn_3B_6O_{12}.3.5H_2O$ were given in Figs. 7, 8, 9 and 10, respectively.

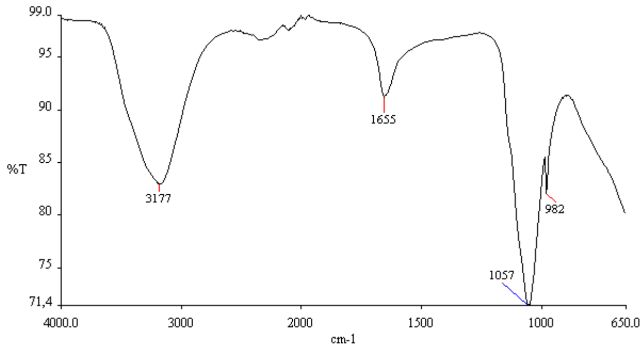

Fig. 7 FT-IR spectrum of $ZnSO_4.7H_2O$

According to the FT-IR inorganic library search, $ZnSO_4.7H_2O$ was found as: "Zinc sulfate heptahydrate ($ZnSO_4.7H_2O$)" with 0.588 score (out of 1) and "AI0167" code.

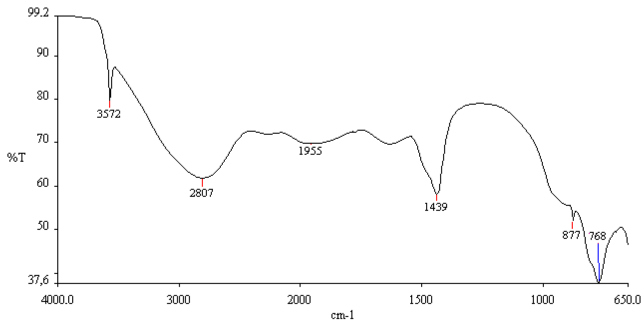

Fig. 8 FT-IR spectrum of NaOH

NaOH was not found in the FT-IR inorganic library search.

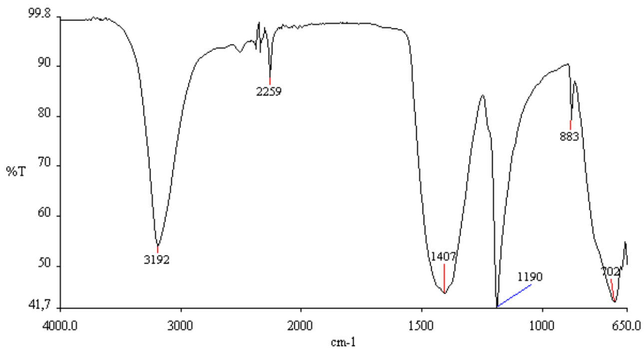

Fig. 9 FT-IR spectrum of H_3BO_3

According to the FT-IR inorganic library search, H_3BO_3 was found as: "Boric acid (H_3BO_3)" with 0.704 score (out of 1) and "AI0031" code.

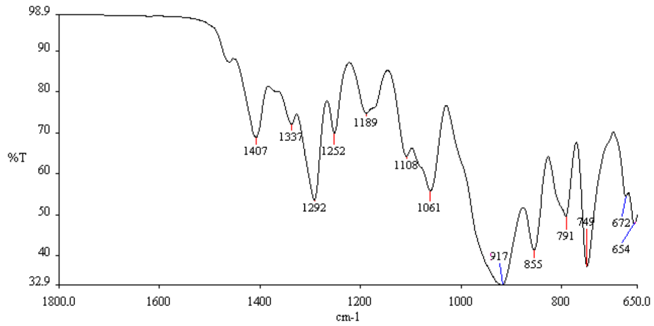

Fig. 10 FT-IR spectrum of commercial $Zn_3B_6O_{12}.3.5H_2O$

Also commercial $Zn_3B_6O_{12}.3.5H_2O$ was not found in the FT-IR inorganic library search, but the boron-oxygen characteristic peaks were observed in the spectrum. The detailed examination will be done at the results section.

B. Synthesized Products

The XRD results of the synthesized zinc borates were given in Table II.

TABLE II
XRD RESULTS OF SYNTHESIZED ZINC BORATES

Molar Ratio (Z:N:H)	Reference code	Mineral Name	Mineral Formula	Score
1:1:1	-	-	-	-
1:1:2	-	-	-	-
1:1:3	00-035-0433	Zinc Oxide Borate Hydrate	$Zn_3B_6O_{12}.3.5H_2O$	72
1:1:4	00-035-0433	Zinc Oxide Borate Hydrate	$Zn_3B_6O_{12}.3.5H_2O$	68
1:2:4	-	-	-	-
1:2:5	00-035-0433	Zinc Oxide Borate Hydrate	$Zn_3B_6O_{12}.3.5H_2O$	72
1:2:6	00-035-0433	Zinc Oxide Borate Hydrate	$Zn_3B_6O_{12}.3.5H_2O$	75

Between the molar ratios of 1:1:1 and 1:1:4 the expected formation occurs at 1:1:3 and 1:1:4, with XRD score of 72 and 68, respectively. The reaction scheme was given in (1):

$$\begin{aligned} &ZnSO_4.7H_2O + NaOH + 3H_3BO_3 + aH_2O \rightarrow \\ &1/6(Zn_3B_6O_{12}.3.5H_2O) + 1/2(Na_2SO_4) + \\ &0.5(ZnSO_4.7H_2O) + H_3BO_3 + bH_2O \end{aligned} \quad (1)$$

From the reaction it is seen that both raw materials used were excess that leaded to lower reaction yields (<50%).

At the second step of the reactions it is decided to increase to molar ratio of NaOH in order to decrease the $ZnSO_4.7H_2O$ from the products. From the XRD results of the second part synthesis, it is seen that in the molar ratio of 1:2:5 and 1:2:6, the formation of zinc borates was accomplished with very high XRD scores of 72 and 75, respectively. The new reaction scheme was given in (2):

$$\begin{aligned} &ZnSO_4.7H_2O + 2NaOH + 6H_3BO_3 + aH_2O \rightarrow \\ &1/3(Zn_3B_6O_{12}.3.5H_2O) + Na_2SO_4 + 4H_3BO_3 + bH_2O \end{aligned} \quad (2)$$

Also the reaction yields were calculated between 95-98% at the molar ratios of 1:2:5 and 1:2:6. The XRD patterns of the zinc borates were given in Figs. 11 and 12, respectively.

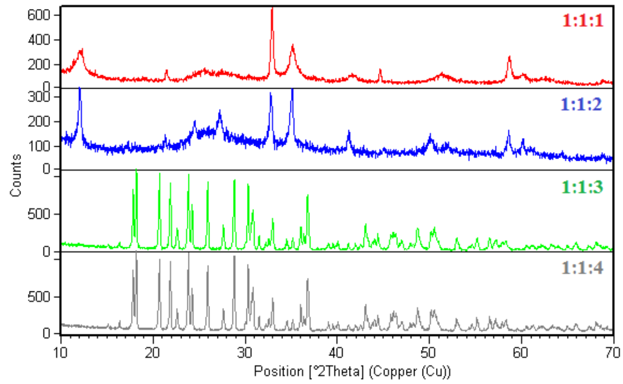

Fig. 11XRD patterns of first step synthesized zinc borates

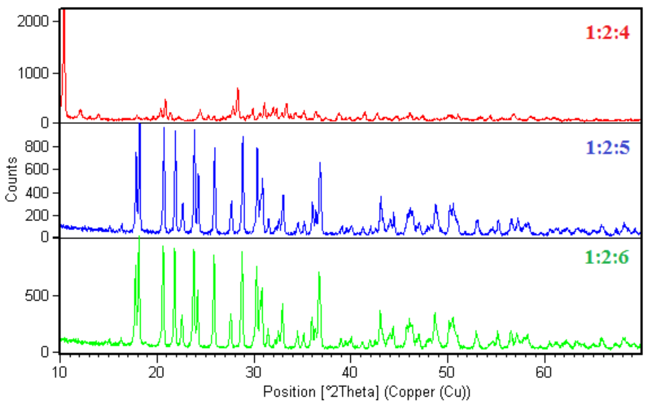

Fig. 12XRD patterns of second step synthesized zinc borates

The FT-IR spectrums and peak interpretations of the synthesized zinc borates were given in Figs. 13, 14 and Table III, respectively.

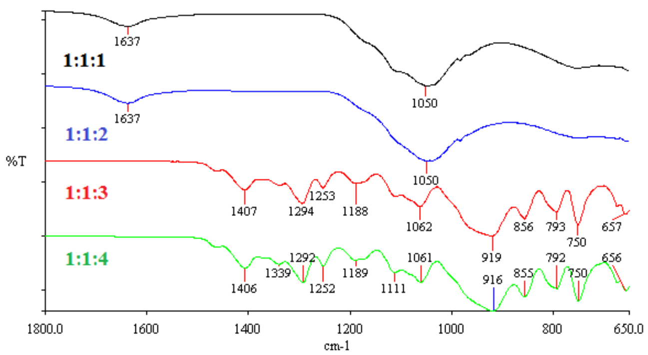

Fig. 13FT-IR spectra of the first step synthesized zinc borates

It is seen that at the molar ratios of 1:1:1 and 1:1:2 the characteristic peaks of zinc borates were not seen.

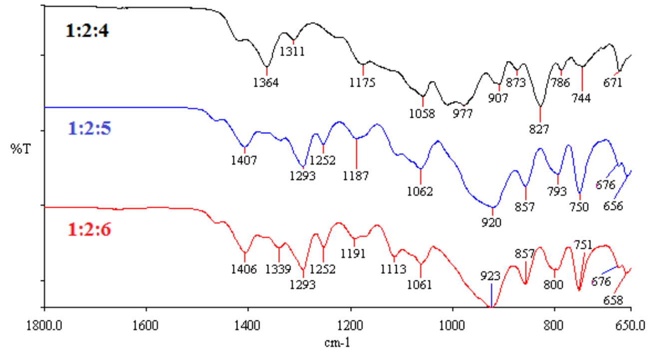

Fig. 14 FT-IR spectra of the first step synthesized zinc borates

Some characteristic peaks were seen of the molar ratio of 1:2:4 but at the ratio of 1:2:5 and 1:2:6 all of the characteristic peaks of zinc borates were matched. At the FT-IR spectra1:1:3, 1:1:4, 1:2:5, 1:2:6 and commercial $Zn_3B_6O_{12}.3.5H_2O$; the peaks between 1407-1252 cm^{-1} represents the three coordinate boron asymmetrical stretching. Bending of (B-O-H) is seen between the peaks of 1191-1111 cm^{-1}. Four coordinate boron asymmetrical and three coordinate boron symmetrical stretching are observed between the peaks of 1062-977 cm^{-1} and 923-873 cm^{-1}, respectively. Between the peaks of 857-786 cm^{-1}, four coordinate boron symmetrical stretching are formed. Last two regions where $\nu_p[B(OH)_4]^-$ and bending of three coordinate boron were seen at the peaks between 751-744 cm^{-1} and 676-654 cm^{-1}, respectively.

TABLE III
FT-IR PEAK INTERPRETATIONS

Peaks (cm^{-1})	Peak Interpretation	Symbol
1778-1424	Bending of H-O-H	δ(H-O-H)
1423-1241	B_3-O asymmetrical stretching	$\nu_{as}(B_3\text{-}O)$
1240-1099	Bending of B-O-H	δ(B-O-H)
1098-958	B_4-O asymmetrical stretching	$\nu_{as}(B_4\text{-}O)$
957-873	B_3-O symmetrical stretching	$\nu_s(B_3\text{-}O)$
872-864	Boric acid characteristic peak	$\nu_p(H_3BO_3)$
863-756	B_4-O symmetrical stretching	$\nu_s(B_4\text{-}O)$
755-677	Characteristic peak of $[B(OH)_4]^-$	$\nu_p[B(OH)_4]^-$
676-642	B_3-O bending	$\delta(B_3\text{-}O)$

IV. CONCLUSION

In this study the optimum molar ratio of the Z:N:H were determined as 1:2:6 for the zinc borate synthesis. The reaction, washing and drying steps are given in 3), (4) and (5), respectively.

Step of reaction

$$ZnSO_4.7H_2O + 2NaOH + 6H_3BO_3 + aH_2O \rightarrow 1/3(Zn_3B_6O_{12}.3.5H_2O) + Na_2SO_4 + 4H_3BO_3 + bH_2O \quad (3)$$

where zinc borate was obtained at crystal phase

Step of washing

$$1/3(Zn_3B_6O_{12}.3.5H_2O) + Na_2SO_4 + 4H_3BO_3 + bH_2O \rightarrow 1/3(Zn_3B_6O_{12}.3.5H_2O) + cH_2O \quad (4)$$

Step of drying

$$1/3\left(Zn_3B_6O_{12}.3.5H_2O\right)+cH_2O\xrightarrow{105^oC}1/3\left(Zn_3B_6O_{12}.3.5H_2O\right) \quad (5)$$

At the future studies, reaction time and the reaction temperature changes will be investigated in the synthesis of zinc borates.

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REFERENCES

[1] M. Gonen, D. Balkose, R. B. Gupta,and S. Ulku, "Supercritical carbondioxide drying of methanolzincboratemixtures", *Ind. Eng. Chem. Res*.,vol. 48, pp. 6869–6876, 2009.

[2] C. Ting, D. Jian-Cheng, W. Long-Shuo, and F. Gang, "Preparation and characterization of nano-zinc borate by a new method", *J. Mater. Process. Tech*.,vol. 209, pp. 4076–4079, 2009.

[3] D. Gürhan, G. Ö. Çakal, İ. Eroğlu, and S. Özkar, Kesikli reaktörde çinkoborat üretiminietkileyenparametrelerinincelenmesi, 1. National Boron Workshop Symposium Book, April 28-29, Ankara, 2005.

[4] D. Schubert, F. Alam, M. Visi and C. Knobler, "Structural characterization and chemistry of the industrially important zinc borate $Zn[B_3O_4(OH)_3]$", *Chem. Mater*.,vol. 15, pp. 866-871, 2002.

[5] H. E. Eltepe, D. Balköse, and S. Ülkü,"Effect of temperature and time on zinc borate species formed from zinc oxide and boric acid in aqueous medium", *Ind. Eng. Chem. Res.*, vol. 46, pp. 2367-2371, 2007.

[6] A. V. Shete, S. B. Sawant, and V. G. Pangarkar, "Kinetics of fluid–solid reaction with an insoluble product: zinc borate by the reaction of boric acid and zinc oxide", *J. Chem. Technol.Biot.*, vol. 79, pp. 526–532, 2004.

[7] X. Shi, Y. Xiao, M. Li, L. Yuan, and J. Sun,"Synthesis of an industrially important zinc borate, $2ZnO{\cdot}3B_2O_3{\cdot}3H_2O$, by a rheological phase reaction method"*Powder Technol*.,vol. 186,pp. 263-266, 2008.

[8] H. Igarashi, H. Sawada, A. Tatebe, and K.Sakao, Patent No: 6780913,U.S.A., 2002.

[9] N. Tugrul, A.S. Kipcak, N. Baran Acarali, E. Moroydor Derun, S. Piskin, "Combined Hydrothermal Synthesis of Zinc and Magnesium Borates at 100°C using ZnO, MgO and H_3BO_3", ICEBESE 2013: International Conference on Environmental, Biological and Ecological Sciences and Engineering, 26-27 September 2013, Rome, Italy.

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