

# Synthesis and Crystal Structure $\text{CoNi}_2(\text{BO}_3)_2$

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**Abstract**—A new metal orthoborate compound, cobalt dinickel orthoborate,  $\text{CoNi}_2(\text{BO}_3)_2$  has been successfully synthesized for the first time. The title compound was synthesized by thermally-induced solid-state chemical reaction at  $900^\circ\text{C}$  between the initial reagents of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{H}_3\text{BO}_3$  which were mixed with the mol ratio of 1 : 2 : 2 respectively. The obtained product was structurally characterized by X-ray powder diffraction technique. It has been found that the  $\text{CoNi}_2(\text{BO}_3)_2$  crystallizes in the kotoite type and isostructural with the compounds having the chemical formula  $\text{M}_3(\text{BO}_3)_2$  where M—Mg, Co and Ni. The synthesized compound belongs to the orthorhombic crystal system with the refined unit cell parameters of  $a = 5.419(9) \text{ \AA}$ ,  $b = 8.352(0) \text{ \AA}$ ,  $c = 4.478(8) \text{ \AA}$  and  $Z = 2$ . The space group was determined as  $Pnmm$ . Further characterizations by FTIR, elemental analysis and thermal analysis were also performed.

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## INTRODUCTION

Borate compounds have been the intensive subjects of crystallographic study for the last century. There is a great interest preparing the anhydrous main group or transition metal borate compounds [1, 2].

Initial works about the structural forms of the several anhydrous orthoborates was reported by Waugh [3] such as  $\text{ScBO}_3$ ,  $\text{InBO}_3$ ,  $\text{GaBO}_3$ ,  $\text{CrBO}_3$ ,  $\text{TiBO}_3$  and  $\text{VBO}_3$  which are the isostructural of the mineral calcite. Another transition metal orthoborate  $\text{Ni}_3(\text{BO}_3)_2$  had been reported by Götz [4] as isomorphous with the cobalt and magnesium orthoborates [5]. Later, Pardo et al. [6] were explained the crystal data of the  $\text{Ni}_3(\text{BO}_3)_2$  in some detail. They obtained the  $\text{Ni}_3(\text{BO}_3)_2$  single crystals by annealing a melt of stoichiometry of  $3 \text{ NiO} \cdot \text{B}_2\text{O}_3$  at  $1200^\circ\text{C}$ .

Effenberger and Pertlik [7] produced and studied the single crystal forms of the three compounds  $\text{M}_3(\text{BO}_3)_2$  (M = Mg, Co and Ni) and compared with crystal system of  $\text{Mn}_3(\text{BO}_3)_2$  [8]. Effenberger et al. Assigned the details of the crystal structures of kotoite type borates which are given again in our article in Figs. 1 and 2. The coordination of B and O atoms in  $\text{M}_3(\text{BO}_3)_2$  (M = Mg, Co and Ni) and the  $\text{BO}_3$  coordination in the kotoite crystal structure of  $\text{Mg}_3(\text{BO}_3)_2$  are given in Figs. 1 and 2, respectively [8]. They found that all of the synthesized metal orthoborates were crystallized in the kotoite form (the kotoite name was given to honor Professor Bundjiro Koto (1856–1935), Japanese geologist, University of Tokyo, Japan, who studied the ore deposits of Hoi Kol, North Korea). In their works

[7],  $\text{Ni}_3(\text{BO}_3)_2$  was crystallized from the starting materials of  $\text{Ni}(\text{OH})_2$  and  $\text{B}_2\text{O}_3$  at  $1100^\circ\text{C}$ . Even though they used different initial reactants they have obtained the same crystal data (orthorhombic system, kotoite type,  $a = 5.396$ ,  $b = 4.459$ ,  $c = 8.297 \text{ \AA}$  and space group  $Pnmm$ ) for the  $\text{Ni}_3(\text{BO}_3)_2$  as reported before by Pardo et al. [6]. Consequently, a collective characteristic of these metal orthoborates have the coordination of the boron

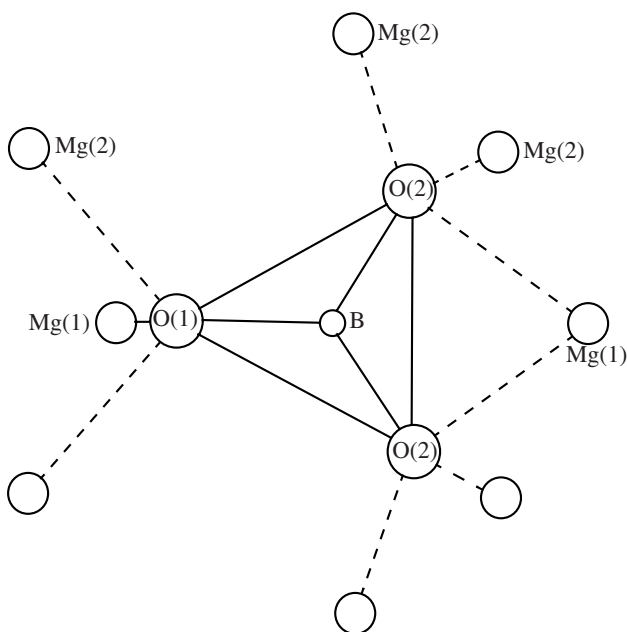


Fig. 1. Coordination of B and O atoms in  $\text{M}_3(\text{BO}_3)_2$  (M = Mg, Co and Ni).

<sup>1</sup> The article is published in the original.

atoms, consisting in discrete trigonal  $\text{BO}_3$  groups in their crystal lattice structures.

Previously we have published a paper [9] related with the binary type metal borate compound,  $\text{Co}_2\text{Ni}(\text{BO}_3)_2$  which was synthesized by thermally-induced solid-state chemical reaction at  $900^\circ\text{C}$  between the chemical reaction of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , and  $\text{H}_3\text{BO}_3$  (mol ratio 2 : 1 : 2). The structural analyses proved that  $\text{Co}_2\text{Ni}(\text{BO}_3)_2$  crystallizes in the kotoite type and isostructural with the chemical formula  $\text{M}_3(\text{BO}_3)_2$  where  $\text{M} = \text{Mg}$ ,  $\text{Co}$  and  $\text{Ni}$ . The synthesized  $\text{Co}_2\text{Ni}(\text{BO}_3)_2$  was belong to the orthorhombic crystal system with the refined unit cell parameters of  $a = 5.444(8)$ ,  $b = 8.404(0)$ ,  $c = 4.504(1)$  Å,  $Z = 2$  and having  $Pnmm$  space group.

In this paper we have reported the crystal system and synthesis procedure of an another new type binary metal borate compound, cobalt dinickel orthoborate,  $\text{CoNi}_2(\text{BO}_3)_2$ .

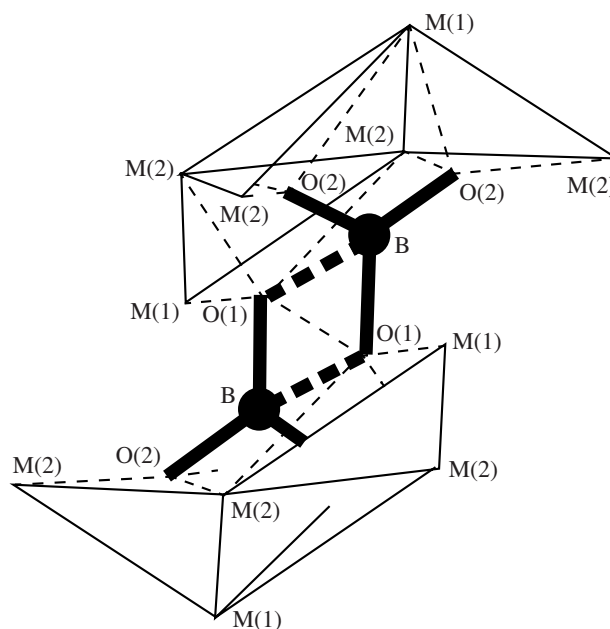
## EXPERIMENTAL

The reagents,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{H}_3\text{BO}_3$  were used as the initial reactants for the synthesis of  $\text{CoNi}_2(\text{BO}_3)_2$ . All the reagents were obtained from the Merck as analytical grade and no further purification was performed.

0.01 mol  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (2.921 g) and 0.02 mol  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (5.837 g), and 0.02 mol  $\text{H}_3\text{BO}_3$  (1.242 g) were weight and mixed. The mixture was grounded homogeneously in a porcelain mortar and transferred into a platinum crucible. Cobalt dinickel orthoborate was synthesized as follows. In the first stage, the furnace temperature was raised up to  $450^\circ\text{C}$  with an increase of  $15^\circ\text{C}$  per minute. The sample was hold for 4 hours at this temperature and later it was cooled down slowly to room temperature. After crushing and blending, it was placed backed to the oven and hold at  $600^\circ\text{C}$  for 3 h period (the furnace was heated from room temp, to  $600^\circ\text{C}$  with an increase of  $1^\circ\text{C}$  per min). Next, the furnace temperature was raised up in the range  $600$ – $900^\circ\text{C}$  with an increase of  $1^\circ\text{C}$  per min. The sample was a final 48-hour hold at  $900^\circ\text{C}$ . Finally, the reaction mixture was allowed to cool down to room temperature with a decrease of  $1^\circ\text{C}$  per min. To get rid of unreacted reagents the final product was washed with hot distilled water and dried at  $60^\circ\text{C}$  for 4 hours. The color of the experimental product is light-brown.

The product was mainly characterized by XRD, FTIR and DTA/TG (Differential Thermal Analysis with Thermo Gravimeter) techniques. Elemental analyses were applied to describe the composition of the experimental product.

The thermally-induced solid-state reactions were carried out by the furnace Protherm PLF 120/10 trademark in the open air.



**Fig. 2.**  $\text{BO}_3$  coordination in the kotoite crystal structure of  $\text{Mg}_3(\text{BO}_3)_2$ .

The XRD data were collected using a Rikagu X-ray diffractometer (Model, Dmax 2200) with the  $\text{CuK}\alpha$  radiation (50 kV, 40 mA,  $\lambda = 1.54059$  Å).

Infrared spectrum was obtained using Mattson Genesis II-FTIR spectrophotometer in  $4000$ – $400$   $\text{cm}^{-1}$  region.

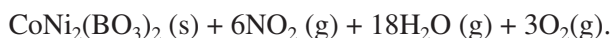
DTA/TG analysis and differential scanning calorimeter was performed using a NETZSCH STA 409. Calibration was conducted in a nitrogen gas atmosphere at a scanning temperature of  $10^\circ\text{C}/\text{min}$ . Calibration of the weight and temperature was performed over the range  $20$ – $1200^\circ\text{C}$ .

The metal ions,  $\text{Co}^{+2}$  and  $\text{Ni}^{+2}$  were analyzed by using UNICAM 929 Atomic Absorption Spectrophotometer (AAS) and the boron analysis were carried out by using Dr. Lange 2800 Spectrophotometer by using a LCK 307 boron cuvette test material (LCK 307 Bor,  $0.05$ – $2.5$  mg/l, supplied from the firm, Hach Lange, GmbH Willstätterstr, 11, 40549 Düsseldorf, Germany).

The refinement of the unit cell parameters was done by the POWD program (an interactive Powder Diffraction Data Interpretation and Indexing Program) [10].

## RESULTS AND DISCUSSION

The chemical reaction for the solid-state synthesis of  $\text{CoNi}_2(\text{BO}_3)_2$  could be given below;



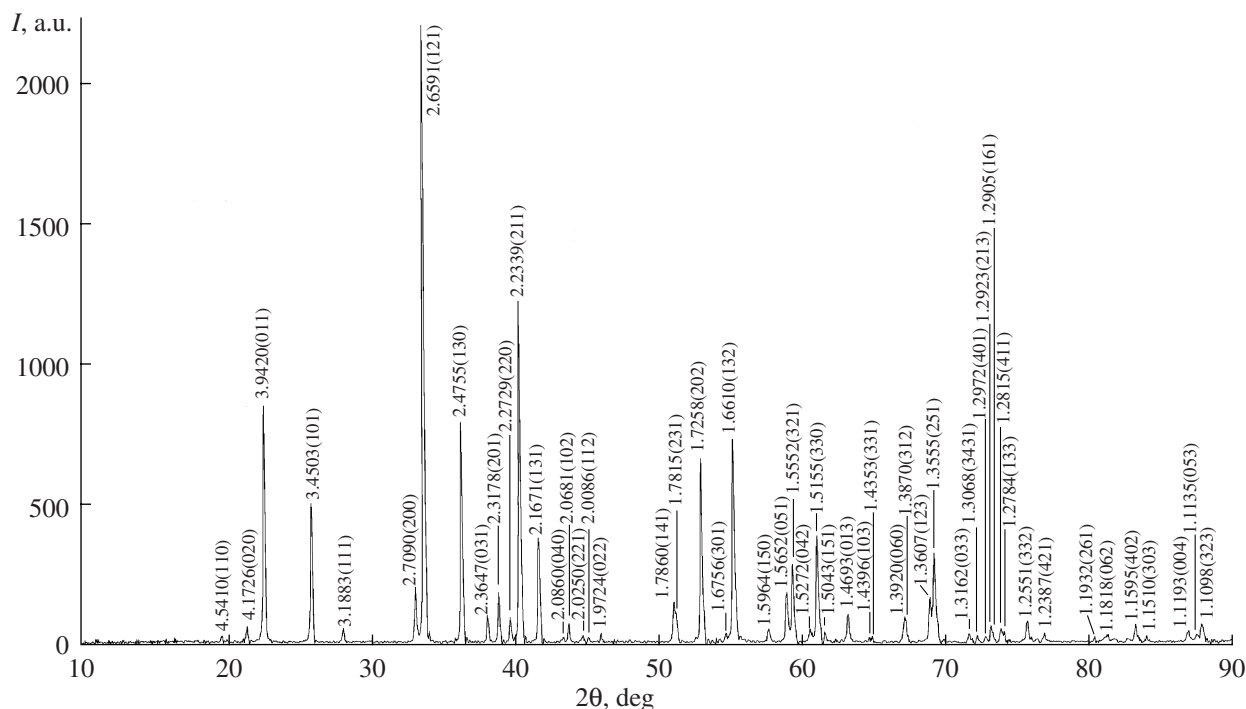


Fig. 3. XRD Pattern of  $\text{CoNi}_2(\text{BO}_3)_2$ .

The crystal system of  $\text{CoNi}_2(\text{BO}_3)_2$  is similar to that of orthorhombic form of  $\text{Ni}_3(\text{BO}_3)_2$  [6] which was crystallized in the orthorhombic system (kotoite type) having a space group  $Pn\bar{m}n$  and with the lattice parameters of  $a = 5.396(2)$ ,  $b = 8.297(1)$ ,  $c = 4.459(1)$  Å and  $Z = 2$  (ICDD 75-1809).

The XRD pattern of the obtained product has been presented in Fig. 3 and the details of the XRD data have been given in Table 1. All peaks in the XRD pattern of the  $\text{CoNi}_2(\text{BO}_3)_2$  can be indexed on the basis of the

orthorhombic system (kotoite type). The refined lattice parameters were calculated as  $a = 5.419(9)$  Å,  $b = 8.352(0)$  Å,  $c = 4.478(8)$  Å and  $Z = 2$ . The space group is determined as  $Pn\bar{m}n$ . The unit cell parameters are slightly higher than  $\text{Ni}_3(\text{BO}_3)_2$  but lower than the  $\text{Co}_2\text{Ni}(\text{BO}_3)_2$  since the stoichiometric ratio of Co atom is twice comparing the  $\text{CoNi}_2(\text{BO}_3)_2$  chemical formula (the radius of  $\text{Co}^{+2}$  ion ( $r = 0.72$  Å) is greater than that of  $\text{Ni}^{+2}$  ion ( $r = 0.69$  Å)) [11]. The crystal system of  $\text{CoNi}_2(\text{BO}_3)_2$  is isostructural with the compounds of  $\text{M}_3(\text{BO}_3)_2$  (where  $\text{M} = \text{Mg}, \text{Co}$  and  $\text{Ni}$ ) [6, 7]. The unit cell parameters,  $Z$  values and densities of the some metal borate compounds having kotoite structure have been given in the Table 2 for comparison purposes.

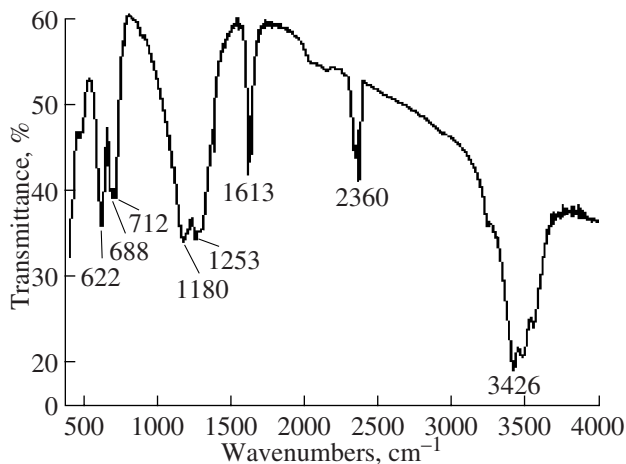


Fig. 4. FTIR Spectrum of  $\text{CoNi}_2(\text{BO}_3)_2$  at room temperature.

The FTIR spectrum of the product is shown in Fig. 4. Some selected IR bands of the functional groups of  $\text{CoNi}_2(\text{BO}_3)_2$  are given in Table 3. Firstly, the peak values were especially compared with the characteristic values of the  $\text{BO}_3^{-3}$  functional group [12, 13]. For the planar, triangular  $\text{BO}_3^{-3}$  group, the wave numbers are in the region  $\nu_3 = 1000\text{--}1300$   $\text{cm}^{-1}$  (asymmetric stretch B–O, broad and strong),  $\nu_1 = 900\text{--}1000$   $\text{cm}^{-1}$  (symmetric stretch B–O, weak),  $\nu_2 = 650\text{--}800$   $\text{cm}^{-1}$  (out-of plane bend sharp and strong) and  $\nu_4 = 450\text{--}650$   $\text{cm}^{-1}$  (in-plane bend, medium). It is clearly shown that the crystal system of  $\text{CoNi}_2(\text{BO}_3)_2$  has mainly had basic structural units of  $\text{BO}_3^{-3}$ .

**Table 1.** The XRD data of  $\text{CoNi}_2(\text{BO}_3)_2$ 

<i>hkl</i>	<i>I</i> / <i>I</i> <sub>0</sub>	<i>d</i> <sub>obs</sub> , Å	<i>d</i> <sub>cal</sub> , Å	<i>d</i> , Å		<i>hkl</i>	<i>I</i> / <i>I</i> <sub>0</sub>	<i>d</i> <sub>obs</sub> , Å	<i>d</i> <sub>cal</sub> , Å	<i>d</i> , Å	
				XRD data of $\text{Ni}_3(\text{BO}_3)_2$ (ICDD 75-1809)						XRD data of $\text{Ni}_3(\text{BO}_3)_2$ (ICDD 75-1809)	
110	1	4.5410	4.5465	4.5235	1	042	2	1.5272	1.5272	1.5186	2
020	2	4.1726	4.1760	4.1485	3	330	17	1.5155	1.5155	1.5078	18
011	38	3.9420	3.9471	3.9277	44	151	2	1.5043	1.5037	1.4943	2
101	23	3.4503	3.4525	3.4372	24	013	4	1.4693	1.4696	1.4630	4
111	2	3.1883	3.1907	3.1755	2	103	1	1.4396	1.4393	1.4329	1
200	9	2.7090	2.7099	2.6980	9	331	1	1.4353	1.4355	1.4283	1
121	100	2.6591	2.6609	2.6467	100	060	4	1.3920	1.3920	1.3828	5
130	36	2.4755	2.4764	2.4612	37	312	3	1.3870	1.3866	1.3803	3
031	4	2.3647	2.3644	2.3502	4	123	7	1.3607	1.3608	1.3544	7
201	8	2.3178	2.3186	2.3083	7	251	14	1.3555	1.3553	1.3473	12
220	4	2.2729	2.2732	2.2617	4	033	1	1.3162	1.3157	1.3092	2
211	55	2.2339	2.2341	2.2238	54	341	1	1.3068	1.3068	1.2998	1
131	17	2.1671	2.1672	2.1547	16	401	1	1.2972	1.2969	1.2912	1
040	1	2.0860	2.0880	2.0742	1	213	3	1.2923	1.2919	1.2861	3
102	3	2.0681	2.0697	2.0605	2	161	2	1.2905	1.2910	1.2829	2
221	1	2.0250	2.0271	2.0171	1	411	2	1.2815	1.2816	1.2758	2
112	1	2.0086	2.0089	1.9998	1	133	2	1.2784	1.2786	1.2723	2
022	1	1.9724	1.9735	1.9638	1	332	3	1.2551	1.2551	1.2490	3
141	6	1.7860	1.7867	1.7759	7	421	1	1.2387	1.2386	1.2328	1
231	5	1.7815	1.7816	1.7721	7	261	1	1.1932	1.1934	1.1862	1
202	30	1.7258	1.7263	1.7186	27	062	1	1.1818	1.1822	1.1751	1
301	1	1.6756	1.6755	1.6680	1	402	3	1.1595	1.1593	1.1541	3
132	33	1.6610	1.6610	1.6523	35	303	1	1.1510	1.1508	1.1457	1
150	2	1.5964	1.5963	1.5860	2	004	2	1.1193	1.1197	1.1147	2
051	8	1.5652	1.5651	1.5552	9	053	1	1.1135	1.1131	1.1071	1
321	13	1.5552	1.5550	1.5476	13	323	3	1.1098	1.1095	1.1044	4

**Table 2.** The cell parameters, Z values and densities of the some metal borate compounds having kotoite structure

Compound and reference	$\text{Mg}_3(\text{BO}_3)_2$ [5]	$\text{Mn}_3(\text{BO}_3)_2$ [8]	$\text{Co}_3(\text{BO}_3)_2$ [5]	$\text{Ni}_3(\text{BO}_3)_2$ [6]	$\text{Co}_2\text{Ni}(\text{BO}_3)_2$ [9]	$\text{CoNi}_2(\text{BO}_3)_2$ Present work
<i>a</i> , Å	5.398(2)	5.658(1)	5.462(2)	5.396(1)	5.444(8)	5.419(9)
<i>b</i> , Å	8.416(2)	8.740(1)	8.436(2)	8.297(2)	8.404(0)	8.352(0)
<i>c</i> , Å	4.497(2)	4.646(2)	4.529(2)	4.459(1)	4.504(1)	4.478(8)
Z	2	2	2	2	2	2
<i>d</i> <sub>exp</sub> , g/cm <sup>3</sup>	3.04	4.00	4.66	4.80	4.608	4.48

The elemental analysis of  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  ions were carried out by using AAS technique. The experimental molar ratio between  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  was found to be 1.05 : 1.95 which is quite acceptable to the atomic mole ratio (1 : 2) for the estimated chemical formula for the  $\text{CoNi}_2(\text{BO}_3)_2$ . The elemental boron analyses were determined by using the azomethine H spectrophotometry method which is one of the good procedures with high

**Table 3.** FTIR Spectrum Data of  $\text{CoNi}_2(\text{BO}_3)_2$ 

Assignments	Frequency, cm <sup>-1</sup> $\text{CoNi}_2(\text{BO}_3)_2$
$\nu_3(\text{BO}_3)$	1253
$\nu_3(\text{BO}_3)$	1180
$\nu_2(\text{BO}_3)$	712
$\nu_2(\text{BO}_3)$	688
$\nu_4(\text{BO}_3)$	622

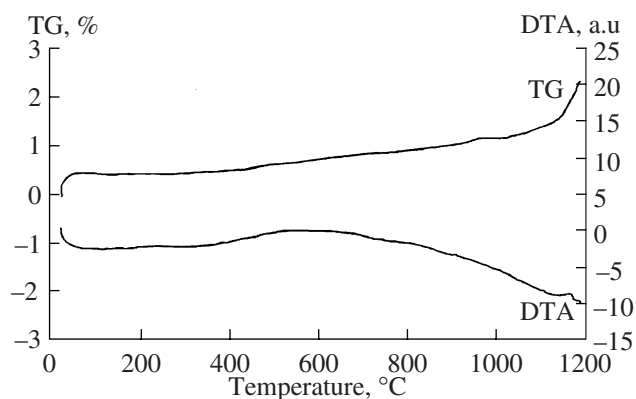


Fig. 5. The simultaneous DTA/TG curves of the experimental product of  $\text{CoNi}_2(\text{BO}_3)_2$ .

sensitivity. The method described detailed in the referred papers [14, 15]. In the process, the borate ions react with azomethine H to form a yellow dye, which is evaluated photometrically. For this process a standard kit was used. Boron concentrations were measured in 1.00 cm quartz sample cells against a reagent blank prepared in a similar manner. The mole ratio of boron had been found experimentally as 1.94 which is very close to the theoretical stoichiometric value of 2.

The density of the product  $\text{CoNi}_2(\text{BO}_3)_2$  was measured by pycnometer using toluen as solvent and found as  $4.4788 \text{ g/cm}^3$ . The experimental  $Z$  value was found as 1.95.

The simultaneous DTA/TG curve of the product is given in Fig. 5. The curves indicate that there is no weight loss and endothermic or exothermic peak from 20 to  $1200^\circ\text{C}$ . Thus, it could be said that the sample is thermodynamically stable within these temperature ranges.

## CONCLUSIONS

A new type cobalt dinickel orthoborate with a chemical formula  $\text{CoNi}_2(\text{BO}_3)_2$  has been synthesized successfully for the first time. The compound was obtained by thermally-induced solid-state chemical reaction between the initial reactants of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{H}_3\text{BO}_3$  which were mixed with the mol ratio of 1 : 2 : 2 in the order. The optimized reaction temperature was assigned as  $900^\circ\text{C}$ . The chemical formula of the cobalt dinickel borate was determined as  $\text{CoNi}_2(\text{BO}_3)_2$  from the XRD, FTIR spectrum and elemental analyses.

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