

Synthesis and crystal structure of dicobalt nickel orthoborate, $\text{Co}_2\text{Ni}(\text{BO}_3)_2$

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Abstract

A new binary metal borate compound, dicobalt nickel orthoborate, $\text{Co}_2\text{Ni}(\text{BO}_3)_2$ has been successfully synthesized by thermally-induced solid-state chemical reaction at 900°C 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 H_3BO_3 (mol ratio 2:1:2). The product was structurally characterized by powder X-ray diffraction technique. $\text{Co}_2\text{Ni}(\text{BO}_3)_2$ crystallizes in the kotoite type and isostructural with the chemical formula $\text{M}_3(\text{BO}_3)_2$ where $\text{M} = \text{Mg}$, Co and Ni . $\text{Co}_2\text{Ni}(\text{BO}_3)_2$ belongs 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 space group was determined as Pnmm. FTIR, elemental analysis and thermal analysis were also discussed in the article.

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1. Introduction

Recently, there is a great interest for the preparing anhydrous main group or transition metal borate compounds [1,2] due to the myriad of structure types attainable by boron's trigonal or tetrahedral coordination. Many metal borates display important practices in nonlinear optical and laser applications [3]. They have also significant magnetic, catalytic and phosphorescent properties [4–7]. Due to the mentioned applications, the metal borates find many technological practices in the industrial arena.

In historical perspectives, the structural forms of the several anhydrous orthoborates were reported by Waugh [8] such as ScBO_3 , InBO_3 , GaBO_3 , CrBO_3 , TiBO_3 and VBO_3 . The common characteristic of these compounds had the isostructural forms with the mineral calcite. Another transition metal orthoborate $\text{Ni}_3(\text{BO}_3)_2$ had been reported by Götz [9] as isomorphous with the cobalt and magnesium orthoborates [10]. Later, Pardo et al. [11] 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 three $\text{NiO} \cdot \text{B}_2\text{O}_3$ at 1200°C .

Effenberger and Pertlik [12] produced and studied the single crystal forms of the three compounds $\text{M}_3(\text{BO}_3)_2$ ($\text{M} = \text{Mg}$, Co and Ni) and compared with crystal system of $\text{Mn}_3(\text{BO}_3)_2$ [13]. They found that all of the synthesized metal orthoborates were crystallized in the kotoite form. The crystal structures of kotoite type borates $\text{M}_3(\text{BO}_3)_2$ ($\text{M} = \text{Mg}$, Co and Ni) are given in details in Figs. 1–3. In their works [12], $\text{Ni}_3(\text{BO}_3)_2$ was obtained from the starting materials of $\text{Ni}(\text{OH})_2$ and B_2O_3 at 1100°C . Even though they used different initial reactants they had obtained the same crystal data (orthorhombic system, kotoite type, a : 5.396, b : 4.459, c : 8.297 Å and space group Pnmm) for the $\text{Ni}_3(\text{BO}_3)_2$ as reported before by Pardo et al. [11]. Consequently, it was concluded that a collective characteristic of these metal orthoborates have the coordination of the boron atoms, consisting in discrete trigonal BO_3 groups in their crystal lattice structures.

In this paper, we have reported the synthesis procedure and the crystal system of the dicobalt nickel orthoborate, $\text{Co}_2\text{Ni}(\text{BO}_3)_2$.

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 H_3BO_3 were used as the initial reactants for the synthesis of $\text{Co}_2\text{Ni}(\text{BO}_3)_2$. They are commercial reagents used without further purification and supplied from the Merck.

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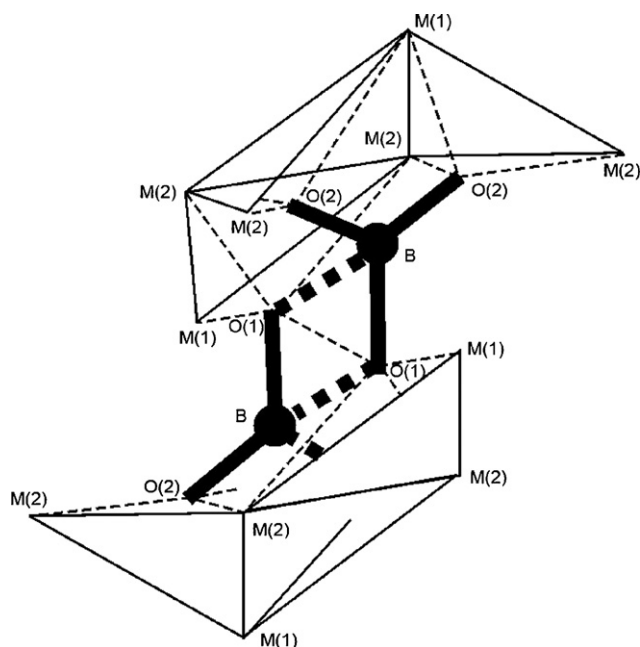


Fig. 1. Coordination of B and O atoms in $M_3(BO_3)_2$ ($M=Mg, Co$ and Ni).

The reactions were carried out by the furnace Protherm PLF 120/10 trademark in the open air. The XRD data were collected using a Rigaku X-ray diffractometer (Model, Dmax 2200) with the $Cu K\alpha$ radiation (50 kV, 40 mA and λ : 1.54060 Å). Infrared spectrum was obtained using Mattson Genesis II-FTIR spectrophotometer in 4000–400 cm^{-1} regions. The metal ions, Co^{2+} and Ni^{2+} were analyzed by using UNICAM 929 Atomic Absorption Spectrophotometer (AAS). Thermogravimetry with differential thermal analysis (TG & DTA) 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 $^{\circ}C min^{-1}$. Calibration of the weight and temperature was performed over the range 20–1200 $^{\circ}C$.

The refinement of the unit cell parameters was calculated by the POWD program (an interactive Powder Diffraction Data Interpretation and Indexing Program Ver. 2.2.) [14].

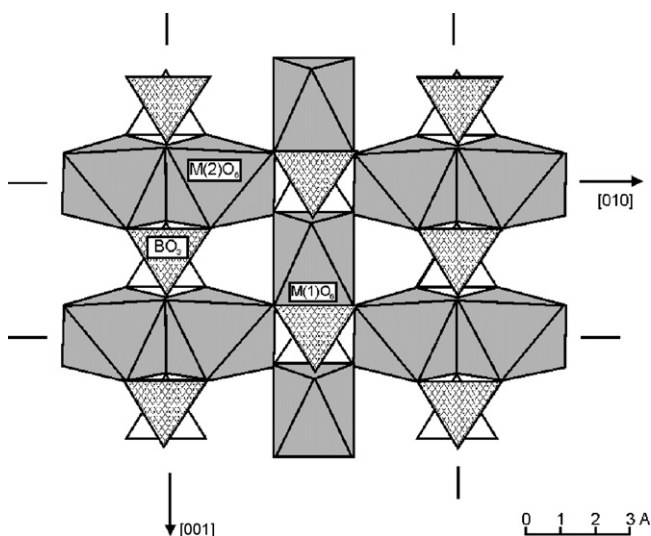


Fig. 2. The crystal structure of $M_3(BO_3)_2$ ($M=Mg, Co$ and Ni) types in projection to parallel to $[1\ 0\ 0]$.

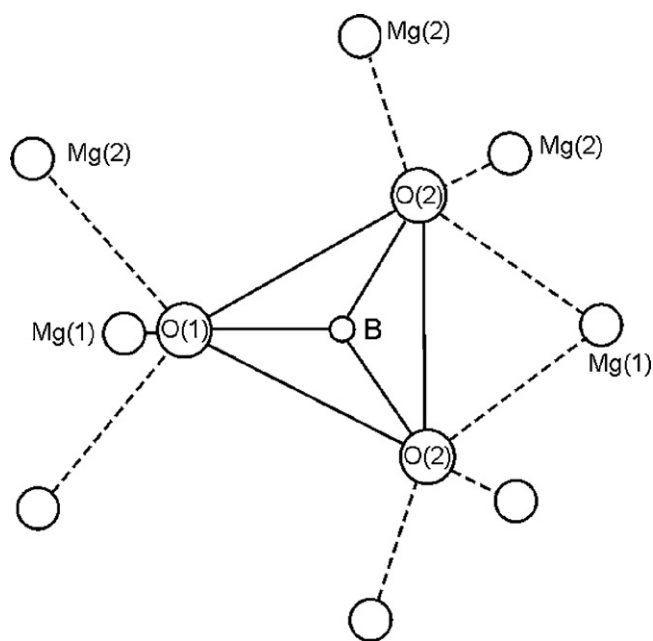


Fig. 3. BO_3 coordination in the kotoite crystal structure of $Mg_3(BO_3)_2$.

The syntheses procedure was realized as follows; 0.02 mol (5.841 g) $Co(NO_3)_2 \cdot 6H_2O$, 0.01 mol (2.918 g) $Ni(NO_3)_2 \cdot 6H_2O$ and 0.02 mol (1.241 g) H_3BO_3 were mixed. The mixture grounded homogeneously in a porcelain mortar. Then the mixture was transferred into a platinum crucible and placed into the furnace. The titled compound was obtained with four steps. Firstly, the temperature was raised up to 450 $^{\circ}C$ with an increase of 15 $^{\circ}C$ per minute. After being held for 4 h at 450 $^{\circ}C$ the sample was taken out from the oven and cooled down and placed to the oven back again after crushing and blending well. Secondly, the temperature was raised up to 600 $^{\circ}C$ with an increase of 1 $^{\circ}C$ per min and the sample was held for 3 h at 600 $^{\circ}C$. In the third stage, the specimen was heated to 900 $^{\circ}C$ with an increase of 1 $^{\circ}C$ per min and was held for 48 h at 900 $^{\circ}C$. Finally, the product was cooled down to the room temperature with a decrease of 1 $^{\circ}C$ per min. Better crystal forms were obtained at 900 $^{\circ}C$. So we determined the optimized temperature as 900 $^{\circ}C$ for the procedure.

To get rid of unreacted reagents the final product was washed with hot distilled water and dried at 60 $^{\circ}C$ for 4 h. The weight of the obtained product was 2.824 g (theoretically 2.942 g was expected). So the yield efficiency was calculated as 96%. The color of product is nearly pink-rose. The synthesized product was mainly characterized by X-ray powder diffraction (XRD) and Fourier Transform IR (FTIR) spectroscopic techniques.

The elemental analysis of Co^{2+} and Ni^{2+} ions were carried out by using Atomic Absorption Spectrophotometer (AAS). The experimental molar ratio between Co and Ni was found to be 1.97:1.03 which is quite agreeable to the atomic mole ratio (2:1) for the estimated chemical formula of $Co_2Ni(BO_3)_2$.

The elemental boron analyses were determined by using the azomethine H spectrophotometric method which is one of the good methods with high sensitivity. The method was described in detail in the referred papers [15,16]. 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 (LCK 307 Bor, 0.05–2.5 $mg L^{-1}$, supplied from the firm, Hach Lange, GmbH Willstätterstr, 11, 40549 Düsseldorf, Germany) 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 1.95 which is very close to the theoretical stoichiometric value of 2.

The density of the product $Co_2Ni(BO_3)_2$ was measured by pycnometer using toluen as solvent and found as 4.608 $g cm^{-3}$. The experimental Z value was found as 1.98 from the refined unit cell parameters which can be accepted as 2. The value is quite agree to the Z values of $Co_3(BO_3)_2$ (ICDD 75-1808) which it is isostructural with the synthesized product $Co_2Ni(BO_3)_2$.

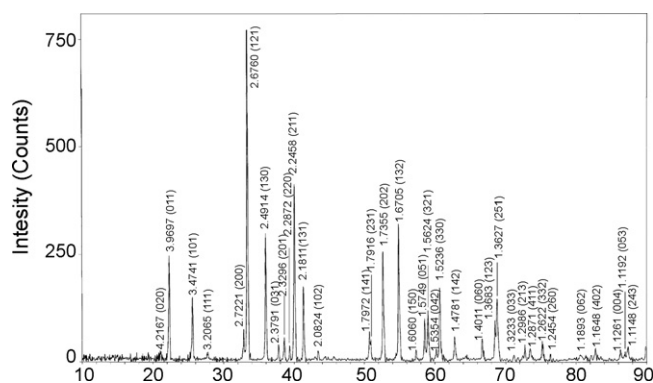
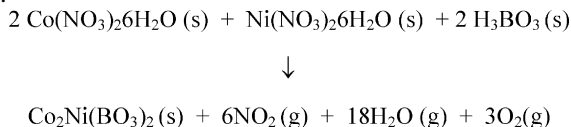


Fig. 4. X-ray powder diffraction pattern of $\text{Co}_2\text{Ni}(\text{BO}_3)_2$.

3. Results and discussion

The basic chemical reaction for the solid-state synthesis of $\text{Co}_2\text{Ni}(\text{BO}_3)_2$ could be suggested by the chemical equation given below, taking into account XRD, FTIR and chemical analyses:



The crystal structure of $\text{Co}_2\text{Ni}(\text{BO}_3)_2$ is very similar to that of orthorhombic form of $\text{Co}_3(\text{BO}_3)_2$ [12]. $\text{Co}_3(\text{BO}_3)_2$ crystallizes in the orthorhombic system having a space group Pnmm and with the lattice parameters of $a = 5.462(2)$, $b = 8.436(2)$, $c = 4.529(2)$ Å and $Z = 2$ (ICDD 75-1808). The XRD pattern of the $\text{Co}_2\text{Ni}(\text{BO}_3)_2$ has been given in Fig. 4 and the details of the XRD data have been presented in Table 1. All peaks in the XRD pattern of the $\text{Co}_2\text{Ni}(\text{BO}_3)_2$ can be indexed on the basis of the orthorhombic crystal system. In the indexing process any impurity phase in the XRD pattern was not detected. The refined lattice parameters were calculated as $a = 5.444(8)$, $b = 8.404(0)$, $c = 4.504(1)$ Å and $Z = 2$. The space group was determined as Pnmm . The calculated refined unit cell parameters are slightly smaller than $\text{Co}_3(\text{BO}_3)_2$ since the radius of Ni^{2+} ion ($r: 0.69$ Å) is smaller than the Co^{2+} ion ($r: 0.72$ Å) [17]. It is also clearly seen that the crystal system is isostructural with the compounds, $\text{M}_3(\text{BO}_3)_2$ ($\text{M} = \text{Mg}, \text{Co}$ and Ni (kotoite type)) which were synthesized synthetically before by Effenberger and Pertlik [12].

The FTIR spectrum of the product is shown in Fig. 5. Some selected IR bands of the functional groups of $\text{Co}_2\text{Ni}(\text{BO}_3)_2$ are given in Table 2. Firstly, the peak values were especially compared with the characteristic values of the BO_3^{3-} functional group [18,19]. For the planar, triangular BO_3^{3-} group, the wavenumbers are in the region ν_3 : $1000\text{--}1300 \text{ cm}^{-1}$ (asymmetric stretch B–O, broad and strong), ν_1 : $900\text{--}1000 \text{ cm}^{-1}$ (symmetric stretch B–O, weak), ν_2 : $650\text{--}800 \text{ cm}^{-1}$ (out-of plane bend sharp and strong) and ν_4 : $450\text{--}650 \text{ cm}^{-1}$ (in-plane bend, medium). It is clearly shown that the crystal system of $\text{Co}_2\text{Ni}(\text{BO}_3)_2$ has mainly had basic structural units of BO_3^{3-} .

The simultaneous TG–DTA curve of the product is shown in Fig. 6. The TG–DTA curves indicate that there is no weight

Table 1
The XRD data of $\text{Co}_2\text{Ni}(\text{BO}_3)_2$

No.	hkl	// I_0	$d_{(\text{obs})}$ (Å)	$d_{(\text{cal})}$ (Å)	XRD data of $\text{Co}_3(\text{BO}_3)_2$ (JCPDS 75-1808)	
					d values	// I_0
1	020	3	4.2167	4.2020	4.2180	3
2	011	32	3.9697	3.9699	3.9903	41
3	101	19	3.4741	3.4705	3.4863	23
4	111	2	3.2065	3.2078	3.2220	2
5	200	9	2.7221	2.7224	2.7310	9
6	121	100	2.6760	2.6759	2.6872	100
7	130	38	2.4914	2.4910	2.5001	37
8	031	5	2.3791	2.3788	2.3889	4
9	201	7	2.3296	2.3299	2.3387	5
10	220	4	2.2872	2.2848	2.2924	4
11	211	53	2.2458	2.2452	2.2537	48
12	131	22	2.1811	2.1798	2.1887	16
13	102	3	2.0824	2.0811	2.0918	2
14	141	9	1.7972	1.7973	1.8045	6
15	231	7	1.7916	1.7913	1.7981	4
16	202	33	1.7355	1.7353	1.7431	26
17	132	41	1.6705	1.6705	1.6783	33
18	150	3	1.6060	1.6060	1.6120	2
19	051	13	1.5749	1.5747	1.5810	9
20	321	15	1.5624	1.5627	1.5681	13
21	042	3	1.5354	1.5363	1.5433	2
22	330	22	1.5236	1.5232	1.5283	16
23	142	7	1.4781	1.4785	1.4860	4
24	060	6	1.4011	1.4007	1.4060	5
25	123	12	1.3683	1.3684	1.3755	7
26	251	19	1.3627	1.3631	1.3683	11
27	033	2	1.3233	1.3233	1.3301	2
28	213	5	1.2986	1.2989	1.3053	3
29	411	4	1.2871	1.2876	1.2919	3
30	332	6	1.2622	1.2617	1.2667	3
31	260	2	1.2454	1.2455	1.2500	1
32	062	3	1.1893	1.1894	1.1944	1
33	402	3	1.1648	1.1649	1.1693	3
34	004	3	1.1261	1.1260	1.1322	2
35	053	2	1.1192	1.1197	1.1250	1
36	243	4	1.1148	1.1145	1.1203	3

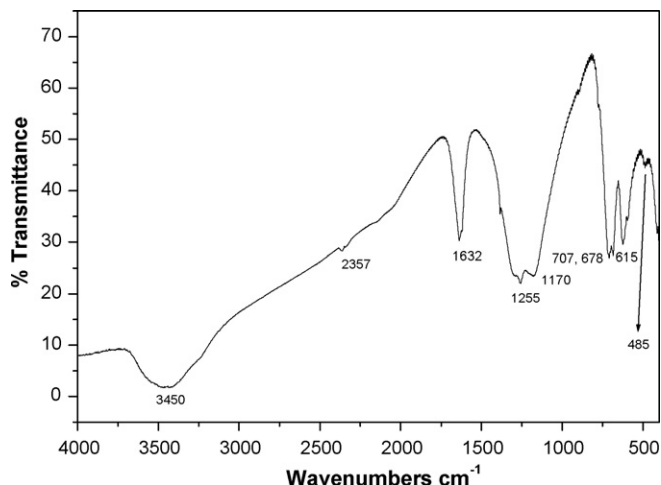


Fig. 5. IR spectrum of $\text{Co}_2\text{Ni}(\text{BO}_3)_2$ at room temperature.

Table 2
FTIR spectrum data of $\text{Co}_2\text{Ni}(\text{BO}_3)_2$

Assignments	Frequency (cm^{-1}) $\text{Co}_2\text{Ni}(\text{BO}_3)_2$
$\nu_3(\text{BO}_3)$	1255
$\nu_3(\text{BO}_3)$	1170
$\nu_2(\text{BO}_3)$	707
$\nu_2(\text{BO}_3)$	668
$\nu_4(\text{BO}_3)$	615
$\nu_4(\text{BO}_3)$	485

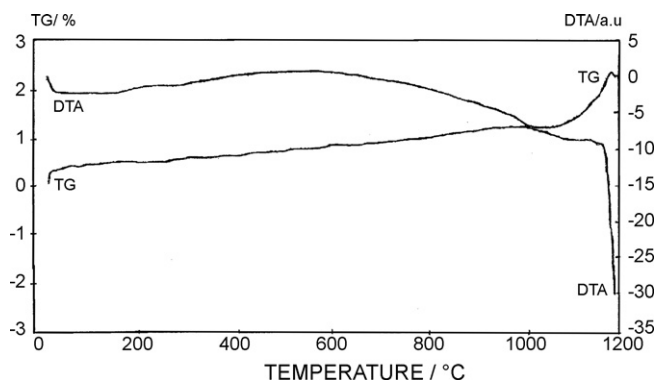


Fig. 6. The simultaneous TG–DTA curves of the experimental product of $\text{Co}_2\text{Ni}(\text{BO}_3)_2$.

loss and endothermic or exothermic peak from 20 to 1200 °C. It could be concluded that the sample is thermodynamically stable within these temperature ranges.

4. Conclusion

A new binary metal orthoborate compound, dicobalt nickel orthoborate with a chemical formula $\text{Co}_2\text{Ni}(\text{BO}_3)_2$ has been synthesized successfully for the first time. The titled 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 H_3BO_3 which were mixed with the mol

ratio of 2:1:2 in the order. The optimized reaction temperature was assigned as 900 °C. The chemical formula of the dicobalt nickel orthoborate was determined as $\text{Co}_2\text{Ni}(\text{BO}_3)_2$ from the XRD, FTIR spectrum and elemental analyses.

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