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# Hydrothermal Synthesis and Structural Investigation of a New Polymorph Form of NdBO<sub>3</sub>

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**Abstract.** The present work deals with the hydrothermal synthesis of a new polymorph form of neodymium orthoborate, NdBO<sub>3</sub>. It was obtained by dissolving 0.1875g B<sub>2</sub>O<sub>3</sub> in 20 ml distilled water and later added to 1.8125 g Nd<sub>2</sub>O<sub>3</sub> and the mixture was transferred to a teflon autoclave. The hydrothermal reaction was performed at 230 °C for 72 h. Characterizations of the sample were carried out by using X-Ray Powder Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR) and Thermal Analysis (DTA/TG) techniques. NdBO<sub>3</sub> was crystallized in monoclinic system and unit cell parameters were calculated as a=11.726(1) Å, b= 6.759(2) Å, c= 9.909(4) Å, β= 114.50(0)°, and space group of C2/c. It was confirmed that NdBO<sub>3</sub> was isostructural with the form of Er doped YBO<sub>3</sub> (a=11.3138(3) Å, b=6.5403(2) Å, c= 9.5499(2) Å and β= 112.902(1)°) at room temperature. The other significant invention of NdBO<sub>3</sub> was thermally stable up to 700 °C, but if the specimen was heated at 780 °C for 4 h, the monoclinic crystal structure was transformed to the aragonite form of NdBO<sub>3</sub> (ICDD 12-756).

**Keywords:** Hydrothermal synthesis, solid state reactions, x-ray powder diffraction

**PACS:** 61.66.Fn

## INTRODUCTION

Since the rare earth orthoborates had some extraordinary optical properties, a great deal of interest has been paid to these types of materials. This quenching phenomenon occurs when active ions get separated from anions like PO<sub>4</sub>, WO<sub>4</sub> and BO<sub>3</sub>, which are big enough. Boron atoms show high structural complexity with the linkage of planar BO<sub>3</sub> and nonplanar BO<sub>4</sub> groups in the crystal systems [1-2].

Initially a scientific group designed and synthesized a new type NdBO<sub>3</sub> with a vaterite form which was obtained from using hydrothermal method by mixing the Nd<sub>2</sub>O<sub>3</sub> and B<sub>2</sub>O<sub>3</sub> compounds with known stoichiometry at 200 °C for one day [3]. The crystal system was characterized by XRD technique and found as hexagonal with the cell parameters a= 3.9008(8) Å and c= 9.0196(6) Å and space group P63/mmc.

Lin et al., [4] in another investigation, studied Er doped YBO<sub>3</sub> which was synthesized by solid-state reaction at 1100°C for 10 h. The powder crystals were analyzed at room temperature and found as monoclinic system with the cell parameters a= 11.3138(3) Å, b= 6.5403(2) Å, c= 9.5499(2) Å and β= 112.902(1)°. The space group was determined as C2/c. The same powder crystals were also characterized by neutron diffraction technique at 1000 °C. The high temperature monoclinic polymorph form was indexed as a= 12.2019(3) Å, b= 7.0671(2) Å, c= 9.3424(2) Å and β= 115.347(1)° with the space group C2/c. In this study, a major evidence discovered was that the boron atoms were tetrahedrally coordinated at room

temperature crystal form (labelled also at low temperature form), whereas at high temperature, all boron atoms were found in a triangular coordination [4].

## EXPERIMENTAL

### Synthesis

The hydrothermal solution was prepared by dissolving 0.1875 g  $B_2O_3$  in 20 ml distilled water and later added to 1.8125 g  $Nd_2O_3$ . Then, the homogeneous mixture had been transferred into autoclave. The top of the autoclave had been closed firmly and kept in the oven at 230 °C for 72 h. In order to remove the impurities, the product had been washed in hot distilled water and then dried in the oven at 60 °C for 4 h.  $NdBO_3$  was obtained in 97 % yield ( 1.0609 g ) as lilac-colored.

### Characterization

The initial reagents of  $Nd_2O_3$  and  $B_2O_3$  have high analytical purity. Hydrothermal reactions have been done in an oven, BINDER ED 53/E2, raised up to maximum 300 °C by using stainless-steel autoclaves covered with teflon in its internal surface and having 45 ml internal volume. The XRD analyses have been done by using an X-ray powder diffractometer of RIGAKU Dmax 2200, works with  $CuK_{\alpha} = 1.54059 \text{ \AA}$ , 30 mA, 40 kV radiation. The infrared spectrum had been taken by using a FTIR spectrophotometer of the PERKIN ELMER BX-2, which work in the 4000-400  $cm^{-1}$  ray range. The thermo gravimetric and differential thermal analysis of the product have been obtained between 20-1200 °C, in the nitrogen atmosphere and with instrument of PERKIN ELMER/DIAMOND TG/DTA, has a 10 °C/minute calibration. The refined unit cell parameters have been calculated with the POWD program (an interactive program for interpreting and indexing powder diffraction data) written down by E. Wu [5].

## RESULTS AND DISCUSSION

The formation mechanism of  $NdBO_3$  in the hydrothermal synthesis is described by Ma et al. [3] as  $B_2O_3$  molecules are dispersed into water by formation of  $H_3BO_3$  at relatively low temperature ( $< 170^\circ C$ ). Later, bulk  $Nd_2O_3$  entirely turns into to nanosize  $Nd(OH)_3$ . Finally, the interaction of nanoparticles  $Nd(OH)_3$  with  $H_3BO_3$  results from the formation of  $NdBO_3$ .

The XRD pattern of synthesized  $NdBO_3$  was given in “Fig. 1”. All peaks “TABLE 1” were indexed in monoclinic system in unit cell parameters  $a = 11.726(1) \text{ \AA}$ ,  $b = 6.759(2) \text{ \AA}$ ,  $c = 9.909(4) \text{ \AA}$ ,  $\beta = 114.50(0)^\circ$ , and space group C2/c. The results justified that crystal form of  $NdBO_3$  was isostructural with the Er doped  $YBO_3$  ( $a = 11.3138(3) \text{ \AA}$ ,  $b = 6.5403(2) \text{ \AA}$ ,  $c = 9.5499(2) \text{ \AA}$  and  $\beta = 112.902(1)^\circ$ ) at room temperature form which was previously reported by Lin et al. [4]. Since the half-diameter of  $Nd^{+3}$  ion ( $r = 1.04 \text{ \AA}$ ) is bigger than  $Y^{+3}$  ion ( $r = 0.92 \text{ \AA}$ ), the unit cell parameters are slightly enlarged [6].

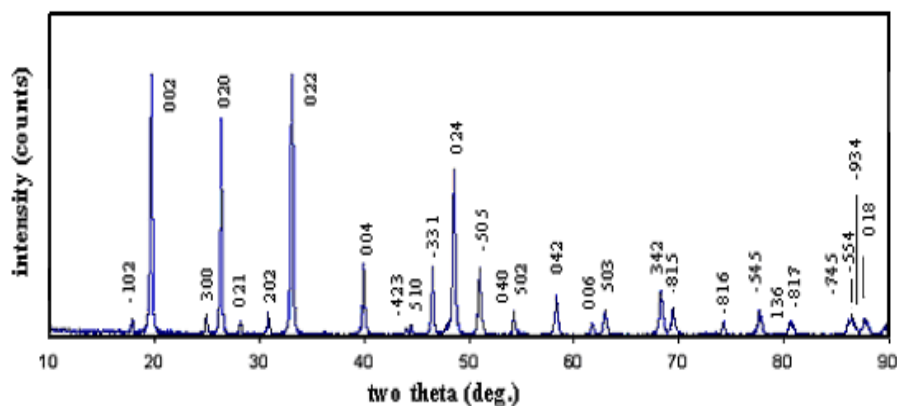
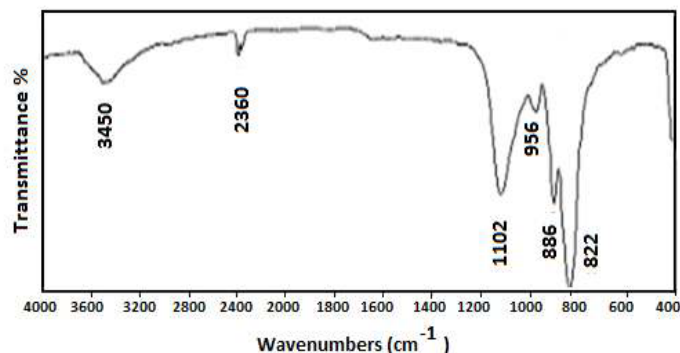


FIGURE 1. XRD Patterns of NdBO<sub>3</sub>.

TABLE 2. XRD Data of NdBO<sub>3</sub>.

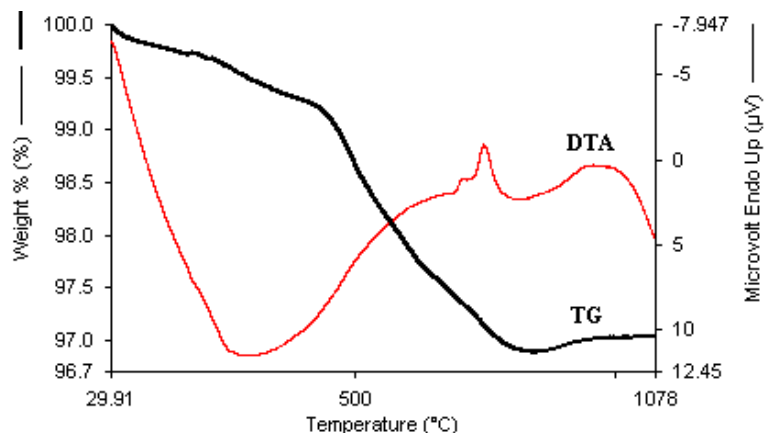
No	$2\theta$	$I/I_0$	$d_{(obs.)}$ (Å)	$d_{(cal.)}$ (Å)	$hkl$	Difference ( $10^{-4}$ )
1	17.879	5	4.9571	4.9545	-102	0.2
2	19.680	91	4.5074	4.5086	002	0.2
3	24.959	7	3.5647	3.5568	300	2.1
4	26.360	77	3.3783	3.3796	020	0.4
5	28.181	5	3.1640	3.1646	021	0.2
6	30.858	8	2.8954	2.9012	202	2.9
7	33.099	100	2.7043	2.7042	022	0.1
8	36.160	1	2.4821	2.4813	410	0.6
9	39.959	27	2.2544	2.2543	004	0.1
10	43.923	3	2.0597	2.0614	-423	2.3
11	44.478	4	2.0353	2.0350	510	0.3
12	46.501	27	1.9514	1.9519	-331	0.8
13	47.902	4	1.8975	1.8956	-215	3.2
14	48.499	63	1.8755	1.8754	024	0.2
15	50.960	26	1.7906	1.7916	-505	2.0
16	54.240	9	1.6898	1.6898	040	0.0
17	54.642	2	1.6783	1.6784	502	0.4
18	58.259	14	1.5824	1.5823	042	0.3
19	61.676	4	1.5027	1.5029	006	0.6
20	62.959	8	1.4751	1.4751	503	0.0
21	68.200	18	1.3740	1.3734	342	2.8
22	69.422	10	1.3527	1.3525	-815	1.0
23	74.179	5	1.2773	1.2772	-816	0.3
24	77.581	10	1.2296	1.2293	-545	2.0
25	80.271	2	1.1950	1.1950	136	0.1
26	80.542	6	1.1917	1.1919	-817	1.4
27	80.801	4	1.1885	1.1885	425	0.1
28	86.139	5	1.1276	1.1277	-745	0.6
29	86.539	6	1.1238	1.1243	-554	3.8
30	86.733	1	1.1218	1.1216	-934	1.5
31	87.701	6	1.1119	1.1118	018	0.9
32	87.919	2	1.1097	1.1097	416	0.1
33	89.600	3	1.0932	1.0932	822	0.1



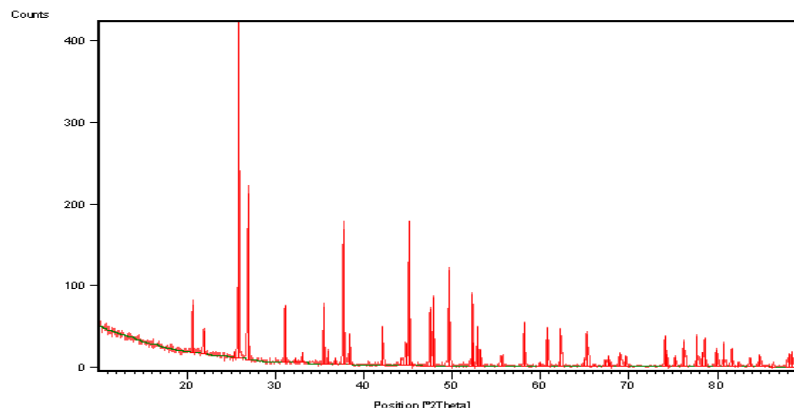
**FIGURE 2.** FTIR Spectrums of NdBO<sub>3</sub> at Room Temperature.

Since the boron may be present in both triangular (BO<sub>3</sub>) and/or tetrahedral (BO<sub>4</sub>) coordination in borate compounds, infrared spectrum could easily determine boron coordination. Specifically, trigonally coordinated boron exhibits strong and broad B-O stretching absorption bands in the 1300-1100 cm<sup>-1</sup> region and tetrahedral boron in the 1100-800 cm<sup>-1</sup> region. In the present work, no peaks in the 1300-1100 cm<sup>-1</sup> region were observed but the peaks were seen in the 1100-800 cm<sup>-1</sup> region. In this respect, boron atoms in the crystal structure were coordinated tetrahedrally instead of trigonally [7-9] “Fig. 2”.

The DTA/TG analysis demonstrates that there is no significant mass loss between 20 and 1200 °C. As it can be seen at the graphics “Fig. 3”, the crystal structure is stable up to 700 °C. But above this temperature, it is pointed out that there exists an exothermic peak at 762 °C. At that temperature a phase transformation was observed. In order to determine this phase, the sample was heated at 780 °C for 4h. The XRD data has been demonstrated that NdBO<sub>3</sub> with monoclinic structure that turns into the arragonite form (NdBO<sub>3</sub> ICDD12-756) by this heating process “Fig. 4”.



**FIGURE 3.** The Simultaneous DTA/TG Curves of NdBO<sub>3</sub>.



**FIGURE 4.** XRD Pattern of heated NdBO<sub>3</sub> Compound (Arragonite Form).

## CONCLUSION

A new polymorph form of NdBO<sub>3</sub> has been obtained for the first time by hydrothermal synthesis technique. The product was obtained in 97 % yield as lilac-coloured. The crystal structure of NdBO<sub>3</sub> was found as monoclinic with the unit cell parameters  $a=11.726(1)$ ,  $b= 6.759(2)$  Å  $c= 9.909(4)$  Å and  $\beta= 114.50(0)^\circ$ , space group C2/c. It was confirmed that NdBO<sub>3</sub> was isostructural with the Er doped YBO<sub>3</sub> ( $a=11.3138(3)$  Å,  $b=6.5403(2)$  Å,  $c= 9.5499(2)$  Å and  $\beta= 112.902(1)^\circ$ ) at room temperature form. The other significant invention of NdBO<sub>3</sub> was thermally stable up to 700 °C , but if the specimen was heated at 780 °C for 4 h, the monoclinic crystal structure was transformed to the aragonite form of NdBO<sub>3</sub> (ICDD 12-756).

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