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COMMENT

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Abstract

The authors of the title paper (Mater. Res. Express 6 (2019) 116213) claim to have grown a nickel boro phthalate (NBP) crystal by the slow evaporation method. A critical analysis of the paper reveals that the so-called NBP is an improperly characterized material. A reinvestigation of the crystal growth reaction has been performed to unambiguously characterize the product. In this letter to the Editor, it is proved that nickel boro phthalate neither contains nickel nor phthalate but is, in fact, boric acid.

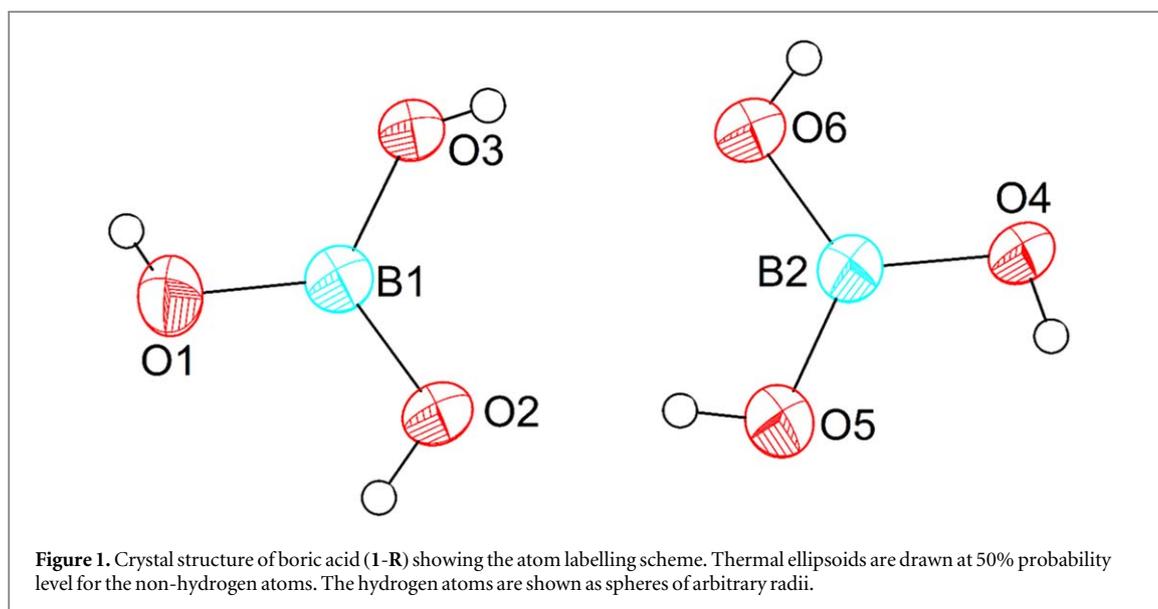
Dear editor

Recently we became aware of the title paper by Divya *et al* [1] published in Materials Research Express. This paper reporting on the growth and properties of a nonlinear optical (NLO) crystal attracted our attention because of an unusual name *viz.* ‘nickel boro phthalate’ for the title crystal. Hence, we perused the title paper to understand what a boro phthalate can be but noticed several inconsistencies in the scientific claims. These are discussed in the following comment to prove that nickel boro phthalate is in fact boric acid.

The authors ended the introduction of the title paper by mentioning, ‘*In the present work, a novel NLO material, Nickel Boro Phthalate (NBP) is grown, and its optical properties are investigated.*’ indicating that NBP is a novel material. The authors of [1] report to have grown the title crystal by a slow evaporation of an aqueous solution containing nickel nitrate, phthalic acid and boric acid in 1:2:2 mole ratio. From the reported reaction scheme, it is noted that the proposed structure of NBP (molecular formula $\text{NiB}_2\text{C}_{16}\text{H}_{10}\text{O}_8$) neither contains phthalate ($\text{C}_8\text{H}_4\text{O}_4$)²⁻ dianion nor hydrogen phthalate ($\text{C}_8\text{H}_5\text{O}_4$)⁻ monoanion and is charge imbalanced (supplementary material (available online at stacks.iop.org/MRX/8/078001/mmedia) Scheme S1). The name boro phthalate is inappropriate for the $\{\text{B}_2\text{C}_{16}\text{H}_{10}\text{O}_8\}$ unit in NBP, which shows an unusual two coordination for Ni(II) and a bond between a carboxylate oxygen and a B-OH moiety of boric acid. In addition, authors report two moles of NO_2 gas as being evolved in this reaction. The picture of the crystal (supplementary material Figure S1) reveals NBP to be a transparent solid with some green patches as can be seen from the non-homogenous colour of the crystal. The authors claim to have characterized this crystal by single crystal x-ray study and spectra.

Under the heading ‘single crystal x-ray diffraction studies’, the authors reported as follows: ‘*The XRD observations reveal that Nickel Boro Phthalate crystal belongs to triclinic crystallographic system with bond lengths $a = 5.90 \text{ \AA}$, $b = 6.38 \text{ \AA}$, $c = 7.93 \text{ \AA}$, and bond angles $\alpha = 77.40^\circ$, $\beta = 88.73^\circ$, $\gamma = 67.63^\circ$ with cell volume as 269 \AA^3 .*’ The lattice parameters a , b and c reported without any esd are incorrectly referred to as bond lengths and the angles α , β and γ as bond angles. The refinement results and CIF file were not reported. A comparison of the unit cell parameters of boric acid [2] and phthalic acid [3] with NBP (Table S1) reveals that the cell volume of NBP is very close to that of boric acid despite the values of a , b , c differing slightly. The volume indicates that the so-called NBP crystal cannot contain twenty-seven non-hydrogen atoms. The situation is very similar to that reported for another so-called thiourea borate crystal which was proved to be a dubious material [4].

The questionable nature of the NBP crystal can be evidenced from the EDAX study where authors reported, ‘*The EDAX spectrum shown in figure 4 confirms the presence of Carbon (38%), Nickel (29%) and Oxygen (27%) in*



the sample is confirmed.' The total % does not add to 100 and the spectrum showing the presence of elements Ba and Tl is a matter of concern (Figure S2). None of the data match with the expected % (in bracket) for the author proposed formula for C (46.80), Ni (14.30), O (31.18), H (2.46) and B (5.26). It is worth mentioning that a block of solid supposed to contain 29% Ni (according to the authors) will be intensely colored but not have some green patches. The presence of any Ni(II) in NBP can be ruled out from the reported optical spectrum, which is transparent in the entire visible region. The authors claim to have performed a second harmonic generation (SHG) experiment and reported 'The characteristic green light was not emitted, indicating the centrosymmetric nature of the crystal'. Despite this, NBP is referred to as a NLO crystal in the title of the paper.

The reported synthesis of NBP in the title paper is quite remarkable due to the claim of NO_2 liberation. Unfortunately, the authors did not consider that phthalate dianion can be formed from phthalic acid by deprotonation of the two $-\text{COOH}$ groups which can be achieved under basic (alkaline) conditions. Besides, the authors did not take into account that either boric acid or phthalic acid or the solvent (water) should function as a reducing agent to reduce the +5 oxidation level of N in nitrate to +4 in NO_2 gas. Since both boric and phthalic acids are not reducing agents, this claim not only contradicts the known chemistry of Ni(II) [5] but is also in disagreement with the reactivity characteristics of Ni(II) salts with phthalic acid [6]. In order to verify if NO_2 liberation takes place during synthesis of NBP two experiments were performed. An aqueous solution of hexa(aqua)nickel(II) nitrate (0.290 g, 1 mmol) was reacted separately with an aqueous solution of phthalic acid (0.332 g, 2 mmol) and boric acid (0.124 g, 2 mmol) respectively. In both these experiments, no NO_2 gas was liberated. The less soluble phthalic acid (or boric acid) could be recovered in near quantitative yields proving no chemical reaction between nickel nitrate and phthalic acid (or boric acid). The recovery of phthalic acid was faster because of its less solubility ($0.6 \text{ g } 100 \text{ ml}^{-1}$) as compared to boric acid ($4.72 \text{ g } 100 \text{ ml}^{-1}$). This was also confirmed by the fractional crystallization of phthalic acid from an aqueous solution containing equimolar amounts of phthalic acid (0.332 g 2 mmol) and boric acid (0.124 g, 2 mmol).

Intending to determine the exact nature of the so-called NBP single crystal, we reinvestigated its crystal growth by taking hexa(aqua)nickel(II) nitrate (0.290 g, 1 mmol) phthalic acid (0.332 g, 2 mmol) and boric acid (0.124 g, 2 mmol) in a 1:2:2 molar ratio in $\sim 75 \text{ ml}$ of distilled water. As reported in the title paper, the reaction mixture was magnetically stirred for 3 h at room temperature. At the end of stirring, the reaction mixture contained suspended matter as mentioned in the title paper. The mixture was left aside for an hour and filtered to obtain 0.325 g colourless powder (1-i). In view of its fine nature and also substantial amount, this material was characterized by i) sodium bicarbonate test and ii) melting point (206.0°C). Based on the brisk effervescence with sodium bicarbonate, which is characteristic of the $-\text{COOH}$ group, the melting point and the yield, the insoluble solid 1-i can be confirmed to be phthalic acid, which is the first product of fractional crystallization.

The pale green filtrate after isolating 1-i was left undisturbed to facilitate slow evaporation of the solvent. After a few days, colourless crystals were obtained. No special efforts were made to grow large crystals since the product had several small x-ray quality crystals. The product was isolated by filtration and washed with little cold water and dried. The product is labelled as compound (1-R). A small crystal was used for crystal structure determination using a Bruker D8 Quest Eco diffractometer. Details of data collection and refinement results are

Table 1. Crystal data and structure refinement for H₃BO₃ (**1-R**).

Empirical formula	BH ₃ O ₃	
Formula weight	61.83	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system, Space group	Triclinic, <i>P</i> $\bar{1}$	
Unit cell dimensions (Å, °)	<i>a</i> = 6.585(2)	α = 119.861(7)
	<i>b</i> = 7.037(2)	β = 91.982(9)
	<i>c</i> = 7.052(2)	γ = 101.398(9)
Volume	274.41(15) Å ³	
Z, calculated density	4, 1.497 mg m ⁻³	
Absorption coefficient	0.154 mm ⁻¹	
F(000)	128	
Crystal size	0.274 × 0.074 × 0.024 mm ³	
Theta range for data collection	3.195 to 28.319°	
Index ranges	-8 ≤ <i>h</i> ≤ 8, -9 ≤ <i>k</i> ≤ 9, -9 ≤ <i>l</i> ≤ 9	
Reflections collected	3718	
Independent reflections	1372 [R(int) = 0.0375]	
Completeness to theta = 25.242°	100%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7457 and 0.6414	
Refinement method	Full-matrix least-squares on F ²	
Data/restraints/parameters	1372/0/94	
Goodness-of-fit on F ²	1.133	
Final R indices [I > 2σ(I)]	R1 = 0.0790, wR2 = 0.2675	
R indices (all data)	R1 = 0.1170, wR2 = 0.2955	
Largest diff. peak and hole	0.316 and -0.435 e.Å ⁻³	
CCDC Number	2061838	

given in table 1. The unit cell of **1-R** (reinvestigated product) is in good agreement with the reported structure of boric acid [2]. Compound **1-R** crystallizes in the centrosymmetric triclinic space group *P* $\bar{1}$. Its structure consists of two crystallographically unique molecules of boric acid with all atoms situated in general position (figure 1).

The checkCIF result of the single crystal study is given in Supplementary material and the CIF file is deposited with the Cambridge Structural Database. The single crystal study reveals that NBP is in fact boric acid. Since this structure is known since 1954 [2] no more description is given. The stepwise fractional crystallization of phthalic acid **1-i** (first product) followed by boric acid also proves that there is no chemical reaction among the three reagents in aqueous solution at room temperature.

The formation of a phthalate free product viz. boric acid in the reinvestigated crystal growth of NBP is not surprising since both nickel(II) nitrate and boric acid are not basic reagents and hence cannot deprotonate phthalic acid. Since boric acid is a centrosymmetric solid it did not give any SHG response. The formation of a nickel free product is in accordance with the optical spectrum in the title paper. Nickel boro phthalate is a new member of improperly characterized crystals based on boric acid the others being 'thiourea borate' [4] barium calcium borate [7] and potassium sodium hydroxide borate hydrate [8] respectively. In view of the improper characterization the other studies on NBP have no scientific merit and are not commented.

Conclusions

In summary, we have proved that a so-called nickel boro phthalate crystal neither contains nickel nor phthalate but is in fact, boric acid (H₃BO₃). The present comment highlights the importance of single-crystal structure determination for compound characterization.

Acknowledgments

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Declaration of conflict of interest

None.

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