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Comments on the paper "Synthesis and characterization of inorganic nonlinear optical material: Potassium sodium hydroxide borate hydrate (KSB) single crystal"

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ABSTRACT

The authors of the title paper (Mater. Lett. **188** (2017) 156–158) claimed to have grown potassium sodium hydroxide borate hydrate (KSB) single crystal and reported its mechanical properties in a subsequent paper (Mater. Lett. **215** (2018) 165–168). In this letter, many points of criticism concerning the crystal growth, structure characterization and interpretation of the spectral and thermal data of the so-called KSB crystal are described to prove that it is a dubious material.

1. Introduction

The authors of the title paper [1] claimed to have grown a so-called potassium sodium hydroxide borate hydrate (KSB) **I**[1] by the slow evaporation solution growth method. However, no molecular formula was reported in the abstract for the alleged new compound **I**, despite a claim of confirming its space group by single-crystal X-ray diffraction. A perusal of the title paper revealed several scientific inconsistencies, which are described in this letter.

2. A so-called potassium sodium hydroxide borate hydrate (I) is a dubious crystal

In the introduction of the title paper, the authors claimed to report on a new class of hydrated borate crystals and mentioned, "*Colourless, perfectly hexagonal shaped crystals have been grown and these crystals are stable at room temperature, which is the advantage of our crystal over the reported one.*" A perusal of the experimental procedure reveals that **I** was grown by slow evaporation solution growth technique using equimolar ratios of potassium hydroxide, sodium hydroxide, malonic acid ($C_3H_4O_4$) and boric acid $B(OH)_3$. The following reaction scheme was proposed for product formation.

$$KOH + NaOH + B(OH)_3 \xrightarrow{C_3H_4O_4} \underset{(\mathbf{I})}{KNaB_4O_5(OH)_4 \cdot 3H_2O} \quad (1)$$

The catalog number of the filter paper was reported instead of the amounts of reagents necessary for obtaining crystals of **I**. Due to insufficient experimental details, **I** cannot be grown by other researchers. Details of the previous method and the advantages of the present procedure (Eq. (1)) for synthesis of **I** are missing in the title paper. From the formula of the product in Eq. (1), it is evident that **I** contains the tetraborate dianion viz. $[B_4O_5(OH)_4]^{2-}$. Tetraborate is a constituent of the minerals borax (disodium tetraborate octahydrate) [2] and tincalconite (disodium tetraborate trihydrate) [3]. Hence **I** cannot be a new class of hydrated borate crystal. Equimolar quantities of KOH, NaOH, $B(OH)_3$ were supposed to have been used to obtain a product containing K, Na and B in 1:1:4 ratio. The role of malonic acid in Eq. (1) and the reason for getting a malonate free tetraborate product are not explained. The authors were unaware that aqueous solutions of tetraborate are quite alkaline. The final reaction mixture (Eq. (1)) cannot be alkaline due to use of equimolar amounts of KOH and NaOH in the presence of the dibasic malonic acid, in addition to $B(OH)_3$, which is a weak acid. The molar ratios of reagents employed and the known chemistry of the reactants rule out the

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[1] Compound is referred to as **I** to avoid use of a long name and a strange code.

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Table 1
Crystallographic data of so-called KSB **I** and a mixed alkali-tetraborate trihydrate **II.**

Compound	Formula	$a = b$ (in Å)	c (in Å)	volume (Å^3)	Space group	Ref
so-called KSB **I**	$KNaB_4O_5(OH)_4{\cdot}3H_2O$	11.35	15.90	1776.07	$P\bar{6}2c$	[1]
II	$K_{1.67}Na_{0.33}B_4O_5(OH)_4{\cdot}3H_2O$	11.278(8)	15.806(10)	1741.07(9)	$P\bar{6}2c$	[5]

formation of any tetraborate containing product. Indeed, all the characterization details provide no evidence whatsoever for the formation of tetraborate, as shown in the following discussion.

Under the heading 'single X-ray diffraction studies' the authors reported, "*The single crystal X-ray diffraction analysis was carried out using direct method and the refinement by full matrix least square technique using SHELXL program*". While describing the mechanical properties of **I** in a later paper [4] the same authors mentioned, "*The unit cell parameter was determined by direct method and the refinement is done by full matrix least square technique using SHELXL program*". However, both publications [1,4] did not report any refinement results of **I** or a CIF file. Instead, the unit cell parameters (without any esd) of **I** (Table 1) and a mixed alkali-tetraborate trihydrate **II** ($K_{1.67}Na_{0.33}B_4O_5(OH)_4{\cdot}3H_2O$) were compared. While reporting on the crystal structure of **II** Smykalla and Behm [5] mentioned that the metastable crystals of **II** were obtained fortuitously. The authors did not consider that K:Na ratio in their formula differs from the ratio of alkali metals in **II** (1:1 in **I** and 5:1 in **II**). The questionable nature of the single crystal structure of **I** can be evidenced from its unit cell volume (1776.07 Å^3), which is more than **II** despite less K content. The results of the single crystal study cannot be relied upon in the absence of a CIF file. It is not clear if any unit cell measurement or structure refinement was really performed. It is unfortunate that **I** was referred to as a new compound in the abstract and a new class of potassium sodium hydroxide borate hydrate in the conclusion.

It is not clear if infrared (IR) spectra were recorded to an accuracy of 0.01 cm^{-1}. The assignments of IR bands based on the work of Wang et al. [6] are incorrect since the compound reported in [6] is a pentaborate dihydrate viz. $Na_2B_5O_8(OH){\cdot}2H_2O$ **III**. It is surprising to note that the authors who compared the unit cell of **I** with that of the mixed alkali tetraborate trihydrate **II**, did not consider it important to compare the IR spectra of **I** and **II**. The reported IR spectrum of **II** [5] does not match with **I** proving both compounds are different. The differing spectra can be explained to use of different materials for unit cell determination and IR spectral study or alternatively a questionable unit cell or both.

In the UV-Vis-NIR discussion, authors claimed that **I** is transparent from 265 to 800 nm. Wang et al. [6] reported that the absorption edge of **III** is less than 190 nm. However, no reason was given for a shift of absorption maximum of **I** to 265 nm. The following explanation for the NLO properties "*In potassium, the p orbitals are actively participate in forming bond with borate system and therefore increase the angular flexibility of the chemical bonds, which enhance the NLO properties*" is inappropriate.

For the formula $KNaB_4O_5(OH)_4{\cdot}3H_2O$, the expected mass loss for three lattice water molecules is 17.58%. In their discussion of thermal data, the authors claim to have observed two weight losses totaling 30.54%, the first of which (~16.04%) was assigned for loss of lattice water and a hydroxyl group. The authors incorrectly assigned the total weight loss in both steps for the loss of both lattice water and hydroxyl groups since they are unaware that the hydroxyl groups in the tetraborate architecture cannot be easily lost unlike lattice water molecules. The thermal data are inconsistent with the formula $KNaB_4O_5(OH)_4{\cdot}3H_2O$.

From the foregoing discussions, it is obvious that compound **I** was formulated based on an incorrect interpretation of the spectral and thermal data. The authors assumed incorrectly that use of equimolar quantities of KOH, NaOH, $B(OH)_3$ and ($C_3H_4O_4$) will result in the formation of a so-called KSB crystal and arbitrarily assigned its formula as $KNaB_4O_5(OH)_4{\cdot}3H_2O$. Due to the absence of a valid experimental proof for the proposed formula, compound **I** should be declared a dubious material. Hence, the dielectric studies in [1] and the mechanical properties of **I** in [4] have no scientific merit.

3. Conclusion

In summary, it is proved that a so-called potassium sodium hydroxide borate hydrate crystal is a dubious material and the publications describing its synthesis and properties [1,4] are completely erroneous.

Declaration of Competing Interest

The author declares that he has no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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