



# Comments on: A remarkable enhancement between optical transparency and SHG efficiency on doped-KHP single crystals

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**Abstract.** The authors of the published title paper (*Bull. Mater. Sci.* 2020 **43** 17) claim to have grown a resorcinol-doped potassium hydrogen phthalate (RKHP) crystal by a slow evaporation method. It was reported that the organic dopant enhances the second harmonic generation efficiency (SHG) of potassium hydrogen phthalate (KHP). In this letter to Editor, many points of criticism concerning the crystal growth and the characterization of the so-called RKHP crystal are discussed to prove that the published original paper is erroneous.

**Keywords.** Crystal growth; potassium hydrogen phthalate; resorcinol; resorcinol-doped KHP crystal.

## 1. Introduction

Recently I became aware of the article by Aarthi *et al* [1] published in the *Bulletin of Materials Science*. In view of my interest in the area of doped crystalline solids [2–5], this article attracted my attention. In recent study, we have shown that the crystal structure of potassium hydrogen phthalate (KHP) consists of parallel chains of face-sharing {KO<sub>7</sub>} polyhedra flanked on either side by hydrogen phthalate wings, which are interlinked by vertex sharing of three polyhedra, resulting in a two-dimensional (2D) coordination polymer [6]. In addition, we showed that a neutral molecule like thiourea cannot be accommodated in this 2D structure. Hence, it was of interest to verify if resorcinol (R) can be incorporated (doped) into the structure of KHP to obtain a so-called RKHP crystal. Therefore, I perused the published article to understand the reported claims. A scrutiny of the publication revealed that the growth and characterization of the so-called resorcinol-doped crystal and the presentation of the results do not meet scientific standards as described below.

## 2. Comments

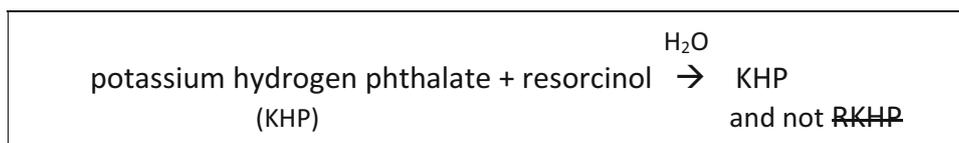
### 2.1 A so-called resorcinol-doped potassium hydrogen phthalate (RKHP) is a dubious crystal

In the introduction, the authors mentioned that their study is focused on elucidating the influence of the organic dopant resorcinol on structural, vibrational, mechanical and non-linear optical properties of KHP crystal and ended the

introduction by stating, ‘An increase in the NLO property is expected due to the decrease of symmetry in the adduct compared to KHP as well as resorcinol.’ However, it is not clear if the article is on a doped or an adduct of KHP crystal, because the experimental begins as follows ‘The pure and resorcinol-doped crystals were synthesized by a slow evaporation technique.’ The so-called RKHP crystal is supposed to have been grown by a slow addition of a calculated amount of resorcinol into a saturated aqueous solution of KHP. No quantities of reagents used for crystal growth and % yield of RKHP obtained are reported in the published title article. Hence, it will be difficult for other researchers to repeat the experiment.

Authors claim to have confirmed the presence of the dopant based on a powder X-ray diffraction (PXRD) analysis and study of infrared (IR) spectra of pure KHP and RKHP. Regarding PXRD analysis, authors reported, ‘From the diffraction peaks, a noticeable variation was observed in the peak intensity of the doped crystal in comparison with that of pure KHP which confirms the influence of dopant ions into the KHP lattice.’ However, the reported pattern especially the indexing of the peaks contradict the above claim, making the following explanation unacceptable ‘A slight variation was observed in the lattice parameters and is due to the lattice distortion by the presence of dopant. Hence, it was confirmed that the grown crystal belongs to the orthorhombic crystal system.’

In IR spectral discussion, a band at 3479 cm<sup>-1</sup> was assigned for the –OH stretching vibration of resorcinol. However, the authors did not consider that KHP contains a –COOH group, which can also exhibit –OH stretching vibration. The reported IR spectra of KHP and RKHP are



**Scheme 1.** Fractional crystallization of KHP.

nearly similar. A better explanation can be that both spectra refer to the same substance, namely KHP, showing the absence of resorcinol. The profile of an IR signal depends on sample preparation and instrumental factors in addition to the molecular symmetry of a given compound. In view of this, it is inappropriate to attribute signal broadening to the presence of dopant. Hence, the claim of Aarthy *et al* ‘Thus, a corresponding broadening of the absorption band with very slight changes in the characteristic peak positions affirms the presence of dopant resorcinol in the parent lattice’ is incorrect.

From the above-mentioned discussion, it is obvious that the characterization of the so-called RKHP crystal is improper. In order to verify if resorcinol can be doped/incorporated into KHP, a crystal growth experiment was performed. Since no mole ratios of the reactants were given, the experiment was performed on a gram scale using commercial reagents in 1:1 ratio. Accordingly, KHP (1.020 g, 5 mmol) and resorcinol (0.550 g, 5 mmol) were dissolved in water. The reaction mixture was filtered and the filtrate was left undisturbed for crystallization. After a few days, ~0.700 g (70%) of crystalline material was isolated. The use of a tenfold excess (10:1) of KHP resulted in the recovery of more than 90% of crystalline product. The IR spectrum of the product showed the absence of phenol and was identical with that of pure KHP. The mother liquor obtained after isolation of the crystals gave an intense coloration with ferric chloride, confirming that no resorcinol whatsoever was incorporated in KHP. The isolation of pure KHP crystals is due to fractional crystallization of the less soluble reagent, while the more soluble resorcinol remains in solution (scheme 1). The non-incorporation of resorcinol is very much in accordance with the 2D architecture of KHP [6].

No reports are available in the scientific literature showing that  $\text{K}^+$  forms compounds with phenols viz.

resorcinol in acidic medium. An aqueous solution of KHP is acidic, which is a well-known primary standard for acid-base titrations [7]. Hence, the improper characterization of the title crystal can be explained as follows: the authors assumed incorrectly that slow evaporation of an aqueous solution containing KHP and resorcinol will result in the formation of a so-called resorcinol-doped KHP crystal without taking into account the chemistry of the reagents employed for the crystal growth study.

### 3. Conclusion

In summary, it is shown that the less soluble potassium hydrogen phthalate fractionally crystallizes from its aqueous solution in the presence of resorcinol. Hence, resorcinol cannot be doped into KHP.

### References

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