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Comments on the paper "Growth, structural, optical and thermal studies of semi-organic nonlinear optical potassium hydrogen oxalate single crystal"

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Abstract

The authors of the title paper (*Appl. Phys. A* **126**, 394 (2020)) report to have grown a new nonlinear optical potassium hydrogen oxalate (KHO) single crystal, which exhibits second harmonic generation (SHG) response. In this comment it is shown that these claims are erroneous since KHO is a well-known solid which crystallizes in the centrosymmetric $P2_1/c$ space group.

Keywords: *crystal growth; potassium hydrogen oxalate; nonlinear optical crystal; erroneous paper*

Recently I read the title paper [1] which is published online in *Applied Physics A*. In the abstract of the title paper authors reported, "*The monoclinic structure with non-centrosymmetric space group $P2_1/c$ of the titular compound has been confirmed by single-crystal X-ray diffraction*" and claimed to have calculated the second-harmonic generation (SHG) efficiency by Kurtz powder method. A perusal of the introduction revealed that in the sequence of oxalates a new semi-organic crystal namely potassium hydrogen oxalate (KHO) has been developed. Authors reported to have grown the KHO crystal using equimolar ratios of potassium hydroxide and oxalic acid and determined that KHO crystallizes in the monoclinic $P2_1/c$ space group. This well-known centrosymmetric space group (No. 14), which accounts for a third of all the crystal structures archived in the Cambridge Structural Database (CSD) [2] is referred to as a non-centrosymmetric space group in the title paper. In the discussion of the single crystal X-ray diffraction analysis the authors reported, "*The obtained lattice parameters of the grown crystal are matches with the reported literature values [19]*" where the citation *[19]* is the paper by Pedersen [3] which reported on the single crystal structure of potassium hydrogen oxalate as early as 1968. It is not clear why the above statement which contradicts the claim of a new semi-organic crystal in the introduction was made. A search of the CSD reveals that this structure is well documented since there are a total of seven hits [4] for potassium hydrogen oxalate including the work of Pedersen (Refcode KHOXAL). It is not clear if authors

of [1] deposited their CIF file in the CSD. The title paper does not mention the new findings not known so far on KHO.

Based on the unit cell parameters reported in [1], which agree with literature data it is obvious that KHO crystallizing in $P2_1/c$ space group is a centrosymmetric solid. Hence such a solid should not give any second harmonic generation (SHG) response. As the authors incorrectly considered $P2_1/c$ as a non-centrosymmetric space group, they performed a Kurtz-Perry powder SHG test and claimed to have observed SHG response (0.81 times of KDP) for KHO. However, this claim is not only erroneous but also unacceptable since centrosymmetric solids cannot exhibit SHG response. In a recent paper [5] we reported that the observation of SHG in ‘‘centrosymmetric crystals’’ can be caused by incorrect determination of crystal symmetry [6] or due to presence of other noncentrosymmetric phases [7, 8] or due to dehydration of hydrated crystals by powdering of the crystal or under laser irradiation [6, 9]. In the present case, it appears the space group is correctly determined. The crystal under study is anhydrous which can rule out the dehydration during laser irradiation. Hence the claim of SHG discovery in KHO is untenable.

In summary, the title KHO crystal cannot be considered as a nonlinear optical crystal and should be declared as a dubious material.

Declaration of Competing Interest None

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