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Comments on the paper “L-Lysine doped Oxalic acid single crystals – A potential phase matchable organic material for optical limiting applications”

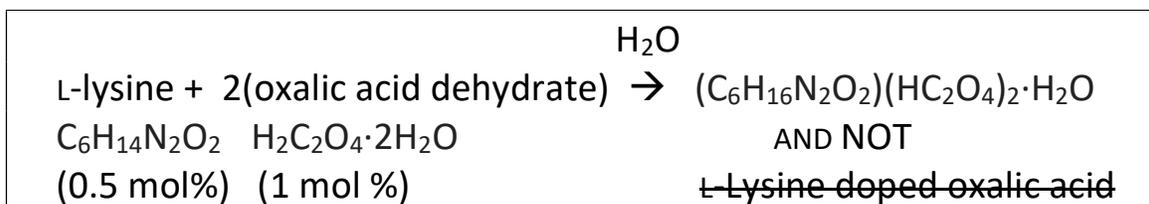
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Graphical abstract

Slow evaporation of an aqueous solution containing L-lysine and oxalic acid in 1:2 mole ratio results in the formation of the noncentrosymmetric L-lysinium(2+) di(hydrogen oxalate) monohydrate crystal and not any compound with $P2_1/n$ symmetry.



Highlights

- # The title paper is critiqued
- # Experimental data reported in the title paper are discussed
- # L-Lysine doped oxalic acid is a dubious crystal

Keywords: *L-Lysine; oxalic acid; L-Lysine doped oxalic acid; dubious crystal; nonlinear optical; improper characterization*

Abstract

The authors of the title paper (*Optics and Laser Technology* **107** (2018) 478–483) report to have grown a so-called ‘L-Lysine doped oxalic acid’ crystal by slow evaporation of an aqueous solution containing L-lysine and oxalic acid in 1:2 mole ratio. In this letter to the Editor, we prove that the ‘L-lysine doped oxalic acid’ is a dubious crystal.

Dear editor,

During a literature survey of amino acid based nonlinear optical (NLO) materials, we read the title paper [1] published in *Optics and Laser Technology*. It is well documented in the literature that L-lysine (or DL-lysine) reacts with oxalic acid forming salts viz. DL-lysinium(+) hydrogen oxalate.2H₂O [2], (bis)-L-lysinium(2+) oxalate di(hydrogen oxalate) [2] and L-lysinium(2+) di(hydrogen oxalate) monohydrate [3]. Hence, the paper describing the growth of a so-called ‘L-Lysine doped oxalic acid’ crystal attracted our attention. A perusal of the publication revealed several scientific inconsistencies in the title paper, which are described in this letter.

The authors of [1] report to have grown undoped or the so-called pure oxalic acid single crystal (1) by slow evaporation method. The title L-lysine doped oxalic acid crystal (2) was grown similarly by slow evaporation of an aqueous solution containing L-lysine (0.5 mol%) and oxalic acid (1 mol%) accounting for a 1:2 mole ratio. It is not clear if the oxalic acid crystals reported in the title paper are anhydrous or hydrated. Two polymorphic modifications of anhydrous oxalic acid [4], two forms each of oxalic acid sesquihydrate [5] and an oxalic acid dihydrate [6] which is commercially available are well documented in the literature (Table 1). The anhydrous and hydrated forms of oxalic acid known to date crystallize in centrosymmetric space groups and are archived in the Cambridge Structural Database (CSD) [7] with the refcodes OXADCH [8] and OXALAC [9].

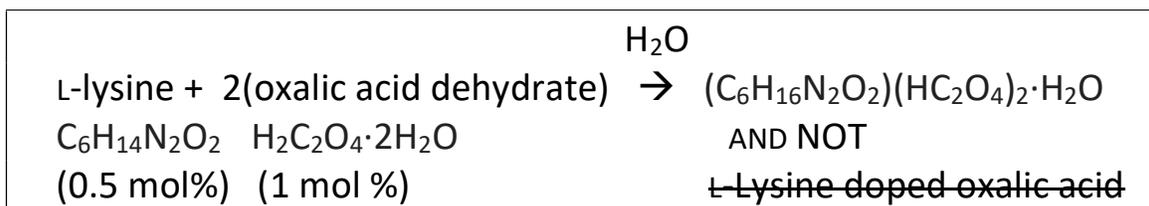
Table 1. Details of structurally characterized anhydrous and hydrated oxalic acid crystals

| No | Name | Formula | Crystal system | Space group | Ref |
|----|---|--|----------------|---|-----|
| 1 | α -oxalic acid | H ₂ C ₂ O ₄ | orthorhombic | <i>Pcab</i> | [4] |
| 2 | β -oxalic acid | H ₂ C ₂ O ₄ | monoclinic | <i>P2₁/c</i> | [4] |
| 3 | oxalic acid sesquihydrate (form I) | H ₂ C ₂ O ₄ ·1.5H ₂ O | orthorhombic | <i>Pnma</i> | [5] |
| 4 | oxalic acid sesquihydrate (form II) | H ₂ C ₂ O ₄ ·1.5H ₂ O | triclinic | <i>P$\bar{1}$</i> | [5] |
| 5 | oxalic acid dihydrate | H ₂ C ₂ O ₄ ·2H ₂ O | monoclinic | <i>P2₁/n</i> | [6] |
| 6 | DL-lysiniun(+) hydrogen oxalate monohydrate | (C ₆ H ₁₅ N ₂ O ₂)(HC ₂ O ₄)·2H ₂ O | triclinic | <i>P$\bar{1}$</i> | [2] |
| 7 | (bis)-L-lysiniun(2+) oxalate di(hydrogen oxalate) | (C ₆ H ₁₆ N ₂ O ₂) ₂ (HC ₂ O ₄) ₂ (C ₂ O ₄) | monoclinic | <i>P2₁</i> | [2] |
| 8 | L-lysiniun(2+) di(hydrogen oxalate) monohydrate | (C ₆ H ₁₆ N ₂ O ₂)(HC ₂ O ₄) ₂ ·H ₂ O | orthorhombic | <i>P2₁2₁2₁</i> | [3] |
| 9 | so-called pure oxalic acid* (1) | --# | monoclinic | <i>P2₁/n</i> | [1] |
| 10 | L-lysine doped oxalic acid* (2) | --# | monoclinic | <i>P2₁/n</i> | [1] |

* No CIF file reported; # No formula; the degree of hydration of oxalic acid is not given

Under the heading single crystal X-ray diffraction analysis, the authors reported that the unit cell parameters of the title crystal were estimated by single crystal X-ray diffraction. However for both the pure as well as the so-called L-lysine doped oxalic acid crystal, the authors did neither report the temperature of unit cell determination nor the esd values of the cell parameters. Since no details of the CIF files of the single crystal work were reported, it is not clear if any structure refinement was really performed. For the so-called pure oxalic acid crystal authors reported, “*It was observed that the material crystallizes in monoclinic symmetry with the space group of P2₁/n.*” The reported cell parameters and space group are in very good agreement with those of the dihydrate proving that the crystal grown is actually the well-known oxalic acid dihydrate. For the doped crystal authors reported, “*In the case of L-Lysine doped oxalic acid, slight shifts were observed in the cell parameters which is due to the incorporation of the dopant. L-Lysine doped Oxalic acid crystals also possesses the noncentrosymmetric P2₁/n with the monoclinic symmetry. The obtained cell values coincide well with the reported*

literature.” This claim is unacceptable for the following reasons: (i) The $P2_1/n$ space group is a centrosymmetric group and not noncentrosymmetric as reported by the authors of [1]. The lattice parameters and the space group of the crystal clearly proves that the crystal studied is oxalic acid dihydrate and not any so-called L-lysine doped oxalic acid. In addition, a solid supposed to contain the chiral L-lysine cannot crystallize in a centrosymmetric space group. (ii) Sukiasyan et al [3] have demonstrated (Scheme 1) that slow evaporation of an aqueous solution containing L-lysine and oxalic acid dihydrate in 1:2 ratio results in the formation of L-lysinium(2+) di(hydrogen oxalate) monohydrate formulated as $(C_6H_{16}N_2O_2)(HC_2O_4)_2 \cdot H_2O$. Hence, the authors of the title paper who claim to have performed a 1:2 (0.5 mol%:1 mol%) reaction should have obtained a noncentrosymmetric salt of L-lysine (entry No. 10 in Table 1) and not a compound with $P2_1/n$ symmetry.



Scheme 1 – Reaction of L-lysine with oxalic acid dihydrate

The infrared (IR) spectrum of the doped crystal contradicts the unit cell study as it is not that of either oxalic acid dihydrate or that of L-lysinium(2+) di(hydrogen oxalate) monohydrate [3, 10]. The incorrect interpretation of the IR spectrum can be evidenced from the spectral discussion wherein authors assign a peak at 1782.07 cm^{-1} for the C=O stretch of urea (-CO-NH-CO) amide in a compound which does not contain urea.

Having incorrectly considered the $P2_1/n$ as a noncentrosymmetric space group the authors performed second harmonic generation (SHG) studies and reported "*From the obtained data the SHG efficiency of undoped and L-Lysine doped oxalic acid sample is 1.4 and 1.5 times that of KDP respectively*". This claim is unacceptable since centrosymmetric solids cannot exhibit

SHG response (see [11] and references therein) and all structurally characterized anhydrous and hydrated compounds of oxalic acid are centrosymmetric. The questionable nature of the SHG claim can be evidenced from the reported *Fig. 5* in the title paper where it can be observed that the curve for undoped sample is higher than L-lysine doped and both are lower than reference material namely KDP.

From the above discussions it is obvious that a so-called pure oxalic acid is actually oxalic acid dihydrate while the L-lysine doped oxalic acid crystal should be considered as an improperly characterized material due to contradictory unit cell and IR spectrum and questionable SHG studies. We believe that the characterization of the L-lysine doped oxalic acid crystal is not based on experimental data but based on an incorrect assumption that slow evaporation of a mixture of oxalic acid and L-lysine in 2:1 ratio will result in a so-called L-lysine doped oxalic acid crystal. In view of the improper characterization, the other studies do not have any scientific merit and hence are not discussed.

In summary, we have shown that the title L-lysine doped oxalic acid crystal is a dubious material.

Declaration of conflict of interest: None

References

- 1] J. Martin Sam Gnanaraj, M. Iniya Pratheep, M. Lawrence, L-Lysine doped Oxalic acid single crystals – A potential phase matchable organic material for optical limiting applications, *Optics and Laser Technology* **107** (2018) 478–483.
- 2] J. Venkatraman, M.M. Prabu, M. Vijayan, X-ray studies on crystalline complexes involving amino acids and peptides. XXXII. Effect of chirality on ionisation state, stoichiometry and aggregation in the complexes of oxalic acid with DL- and L-lysine, *J. Peptide Res.* **50** 77-87 (1997).
- 3] R.P. Sukiasyan, H.A. Karapetyan, A.M. Petrosyan, L-Lysine dioxalate, *J Mol Struc* **888** 230-237 (2008).
- 4] J.L. Derissen, P.H. Smit, Refinement of the Crystal Structures of Anhydrous α - and β -Oxalic Acids, *Acta Crystallogr.* **B30** (1974) 2240-2242.
- 5] M. Wenger, J. Bernstein, Cocrystal Design Gone Awry? A New Dimorphic Hydrate of Oxalic Acid, *Molecular pharmaceutics*, **4** (2007) 355-359.
- 6] T.M. Sabine, G.W. Cox, B.M. Craven, A neutron diffraction study of α -oxalic acid dihydrate, *Acta Crystallogr.* **B25** (1969) 2437-2441.
- 7] C.R. Groom, I.J. Bruno, M.P. Lightfoot, S.C. Ward, The Cambridge Structural Database, *Acta Crystallogr.*, **B72** 171-179 (2016).
- 8] <https://www.ccdc.cam.ac.uk/structures/Search?Ccdcid=OXACDH&DatabaseToSearch=Published>
- 9] <https://www.ccdc.cam.ac.uk/structures/Search?Ccdcid=OXALAC&DatabaseToSearch=Published>
- 10] R.P. Sukiasyan, New salts of L-lysine. In: Proc. Conf. Laser Physics-2004, October 12–15, 2004, Ashtarak, Armenia, 2005, p. 105-108.
- 11] B.R. Srinivasan, N.U. Parsekar, R.A. Apreyan, A.M. Petrosyan, On the second harmonic generation activity in centrosymmetric crystals, *Molecular Crystals & Liquid Crystals*, **680** (2019) 75-84.