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Comments on "Investigation on novel bulk size single crystal of Glycine with metal ions grown by solution growth method for photonic applications"

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ABSTRACT

The authors of the title paper (Materials Letters **257** (2019) 126674) report to have grown a glycine potassium dichromate (GPDC) single crystal by slow evaporation of an aqueous solution containing equimolar quantities of glycine and potassium dichromate. In this comment, many points of criticism, concerning the crystal growth and experimental data for this so-called GPDC crystal are discussed to prove that it is a dubious material.

1. Introduction

The study of amino acids and their compounds is an area of topical research [1]. Unlike other naturally occurring amino acids glycine is achiral and exhibits polymorphism. Although two (*viz.* β- and γ-glycine) of the three crystal forms known at usual conditions (α, β and γ) are non-centrosymmetric, a majority of the known glycine based compounds archived in the Cambridge Structural Database (CSD) [2] are known to crystallize in centrosymmetric space groups. Disregarding this structural aspect and a wrong interpretation of experimental data by some research groups has resulted in the publication of several improperly characterized glycine based crystals as novel nonlinear optical materials. In several publications including a case study [3–6], it was demonstrated that the improper characterization is due to formulating the so-called 'new crystal' based on an unit cell measurement instead of a structure refinement. Despite the publication of several critical comments proving that several glycine based crystals are dubious materials, erroneous claims continue to get published in reputed international journals, for example, the title paper reporting the growth and characterization of a so-called glycine potassium dichromate **I** (GPDC) single crystal [7]. In order to avoid the use of a strange code GPDC, it is identified as compound **I** throughout this paper. No example of a structurally characterized dichromate compound containing glycine is available in the CSD [2]. Hence the title paper on **I** displaying a big block of red crystal attracted our intention and was perused to verify the claim. In the following comment, we show that **I** is a dubious crystal.

2. Comments

The authors of the title paper report on having grown single crystals of **I** by slow evaporation of an aqueous solution containing equimolar ratios of glycine and potassium dichromate ($K_2Cr_2O_7$). No quantities of reagents employed for crystal growth, as well as the amount of **I** obtained, are specified. Despite a claim of structure having been determined by single-crystal study, the molecular formula of **I** is missing in the entire paper. Instead, a strange code GPDC is used for compound identification. The questionable nature of **I** can be first evidenced from the assignments of the infrared spectrum for the stretching and bending vibrations of $-NO_2$ since neither glycine nor $K_2Cr_2O_7$ contains any nitro group. The assignment of the band at 448 cm^{-1} to K-O stretching vibration is incorrect because K…O contact is not a covalent bond. A scrutiny of the IR spectrum reveals the absence of glycine in **I**. Regrettably, the spectrum matches perfectly with the IR spectrum of $K_2Cr_2O_7$ contradicting the authors' claim of having grown a novel crystal. In their discussion of X-ray diffraction analysis, authors reported '*It was observed that the crystal belongs to Triclinic system with the following cell dimensions "a = 7.412 Å, b = 8.501 Å, c = 12.471 Å, α = 96°, β = 97°, γ = 90, and volume 785 Å^3 with Non-Centro symmetric*

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space group P.' The unit cell parameters (without any esd) of **I** appear to differ from the α-form of $K_2Cr_2O_7$ (*a = 13.367(11) Å, b = 7.376(5) Å, c = 7.445(5) Å, α = 90.75(5)°, β = 96.21(7) °, γ = 97.96(5) V = 722.3 Å^3)* [8]. Still compound **I** cannot be considered as a novel crystal, due to i) the dubious space group and ii) the absence of a CIF file to support the single crystal analysis. The findings from the UV–Vis spectral data should be termed quite remarkable. Although the authors mentioned, "*The resultant spectrum shows that the crystal has very low absorbance in the entire visible and IR region,*" this is unacceptable because a red crystal is expected to absorb in the visible region. We believe that the spectrum actually represents glycine, which is transparent in the visible region. The use of glycine for UV–Vis spectral study gains credence from the SHG results as the gamma modification of glycine is a non-centrosymmetric solid while the room temperature modification of $K_2Cr_2O_7$ crystallizes in the centrosymmetric triclinic space group $P\bar{1}$. The spectra indicate that there is no chemical reaction between potassium dichromate and glycine and the less soluble $K_2Cr_2O_7$, has fractionally crystallized. The possibility that authors obtained a mixture of $K_2Cr_2O_7$ and γ-glycine due to total evaporation of water cannot be ruled out.

In their discussion of UV–Vis-NIR analysis, the authors reported, "*We are comparing the energy band gap values with other same class crystals like Tris-Glycine Zinc chloride [14] and Glycine picrate [15] is 4.60 eV and 3.7 eV*". However, both these citations *[14]* and *[15]* do not pertain to what the authors claim. In fact, the citation *[15]* is on $3Gly.ZnCl_2$ (Gly = glycine) and not on so-called "glycine picrate", while *[14]* reports on a so-called "glycine manganous acetate". Regrettably seven of the fifteen citations are irrelevant to the subject matter as these have nothing to do with glycine or dichromate. Considering the contradictory nature of the IR spectrum, unit cell, UV–Vis spectrum, and SHG result, **I** can be declared as a new dubious crystal.

3. Conclusion

In this comment, we have proved that the title paper is completely erroneous. Our present comment once again highlights the importance of single-crystal structure refinement for new compound characterization. We do hope that leading journals will make structure determination an essential pre-requirement for the publication of "new crystals".

CRediT authorship contribution statement

Bikshandarkoil R. Srinivasan: Conceptualization, Writing - review & editing. **Aram M. Petrosyan:** .

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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