Comment on "A study on the growth and characterization of zinc sulphate mono hydrate doped glycine NLO single…

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Comments on the paper "A study on the growth and characterization of zinc sulphate mono hydrate doped glycine NLO single crystals"

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Abstract

We prove that a so called zinc sulphate mono hydrate doped glycine NLO single crystal described by Sakuntala et al (Ferroelectrics 504 (2016) 96-103) is a dubious crystal.

Keywords*: glycine; zinc sulphate mono hydrate doped glycine; dubious crystal; erroneous paper*

Comment

One normally expects authors of a research article to be aware of the status of the scientific literature in the area of study. Of the amino acid based materials a large number of dubious crystals are based on glycine [1-9]. Starting from a case study of salts of amino acids in 2010 [1] where the glycine / zinc sulphate / water reaction system was described in detail several critical comments have been published in the literature showing that many claims of growth of NLO crystals based on glycine are completely erroneous. In most cases, the claimed novel nonlinear optical (NLO) crystal was proved to be one of the polymorphic modifications of glycine. For example, in a recent comment we proved that a so called diglycine ammonioum sulphate crystal is actually γ-glycine crystal [9]. Although the reasons for the growth of the title crystal by the authors of [10] despite the publication of a case study [1] are not very clear, it can be easily proved that the title crystal is actually α-glycine.

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The authors of the title paper claim to have grown a so called zinc sulphate mono hydrate doped glycine NLO single crystal **1** from saturated solutions of $ZnSO_4 \cdot H_2O$ and glycine. The references in the title paper [10] show that the authors are not familiar with relevant literature, for example, the work on the non-centrosymmetric glycine zinc sulfate trihydrate [11]. Since no quantities of reagents taken and the yield of the title crystal obtained are given, it is difficult for other researchers to perform the crystal growth experiment. Based on their single crystal data of pure glycine (V= 308.62Å^3) and as grown crystal of **1** (V= 308.43Å^3) where the authors could determine the space group as $P2_1/n$, authors declared that they have grown a doped crystal based on the minor changes in the unit cell parameters. However, authors did not take into account that the volume of the so called doped crystal shows a negligible change indicating that no zinc sulphate is actually incorporated into the crystal structure. That no doping has taken place is revealed by a comparison of the X-ray powder pattern of pure glycine and the as grown crystal **1**. In fact, the best scientific explanation of the powder pattern is that the as grown crystal is phase pure which perfectly matches with that of α-glycine.

It is very unfortunate that the authors of the title paper are not aware of a basic property of NLO crystals namely materials crystallizing in centrosymmetric space groups cannot exhibit any second harmonic generation (SHG) and hence should not be labeled as NLO crystals. Although it is not clear as to why the authors decided to study the SHG output of **1** despite knowing that $P2_1/n$ is a centrosymmetric space group, the authors claim of 50% SHG output of KDP for **1** is not only unacceptable but also raises serious concern about the entire research. The observation of SHG can be explained e.g. the crystal used for SHG and unit cell are not one and the same. The incorrect interpretation of the unit cell and powder pattern and other data by the authors and a study of the SHG response for a $P2_1/n$ crystal prove beyond doubt that the title paper is completely erroneous. Hence the title crystal **1** is to be declared as a DUBIOUS crystal in the glycine family.

In summary, we are very disappointed to mention that journals with high reputation publish such a fundamentally wrong paper after a peer review process. We hope that the present comment will help to reduce (if not stop) the publication of erroneous papers in the area of crystal growth of nonlinear optical materials.

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