For the published version please see https://doi.org/10.1016/j.matlet.2020.127684

Comments on "Selective enhancement of second and third-order nonlinear optical properties of newly synthesised trisglycine epsomite single crystal"

Bikshandarkoil R. Srinivasan

School of Chemical Sciences, Goa University, Goa 403206, India Email: srini@unigoa.ac.in

Highlights

The title paper is commented

Many points of criticisms are highlighted

Experimental data reported in the title paper are discussed

Trisglycine epsomite is a DUBIOUS CRYSTAL

Abstract

The authors of the title paper (Materials Letters **223** (2018) 33–36) report to have newly synthesized trisglycine epsomite (TGE) single crystals by conventional solution growth method. In this comment, many points of criticism, concerning the crystal growth and experimental data of this so-called TGE crystal are discussed to prove that trisglycine epsomite is a dubious crystal.

Keywords: *Crystal growth; Optical properties; glycine; trisglycine epsomite; dubious crystal; Tetraaquadiglycinemagnesium(II) hexaaquamagnesium(II) bis(sulfate)*

Introduction

During a literature survey of glycine based compounds, the title paper [1] reporting on the enhancement of the optical properties of newly synthesised trisglycine epsomite (TGE) single crystal attracted my attention due to the highlight "*TGE crystal structure altered from orthorhombic to triclinic*". In the abstract the authors reported "*Single crystal XRD confirms the distortion of crystal structure from orthorhombic to triclinic with space group*". Hence, I perused the paper to better understand the above findings. However, the scrutiny revealed no explanation for the distortion of the crystal structure in the entire publication. In addition, several inconsistencies were observed in the scientific claims, which are described in the following comment.

Comment

Epsomite refers to a mineral of formula $MgSO_4 \cdot 7H_2O$. Hence the composition of trisglycine epsomite **1** (called as TGE by authors) can be given as $[(Gly)_3MgSO_4(H_2O)_7]$ (Gly = glycine). However, no formula whatsoever can be seen in the entire manuscript. To avoid use of a long formula or a strange code TGE, it is referred to as compound **1** in this comment. The authors of [1] report to have grown crystals of **1** by slow evaporation of an aqueous solution containing glycine and $MgSO_4$ in 3:1 mole ratio. No quantities of reagents employed for crystal growth and % yield of **1** obtained are given. Under the heading single-crystal X-ray diffraction study, the authors mentioned that **1** crystallizes in the triclinic noncentrosymmetric space group $P\bar{1}$ and reported only the unit cell dimensions without any esd. In addition to the fact that the authors are unaware that $P\bar{1}$ (space group No. 2) is a centrosymmetric space group, the claim that their lattice parameters are in good agreement with the reported values *'[5]'* contradicts the title and also the last sentence in the introduction "*In this present investigation for the first time we have reported the growth, spectral, optical, SHG, TONLO and SEM properties of TGE*".

The citation *'[5]'* by Elayaraja *et al*. [2] is a report on the crystal structure of tetraaquadiglycinemagnesium(II) hexaaquamagnesium(II) bis(sulfate). This compound represented by the formula $[Mg(H_2O)_4(Gly)_2][Mg(H_2O)_6](SO_4)_2$ **2** is the only known structurally characterized

Mg(II) material containing both glycine and sulfate and is a member of a series of isostructural metal-glycine compounds [3, 4]. The metal:glycine ratio in **2** is 1:1 and this well-known compound is prepared using glycine and $MgSO_4$ in equimolar (1:1) ratios from an aqueous solution [2, 3]. The identical unit cells, once again shows that from the $MgSO_4$ / glycine / water system no new compound other than **2** can be obtained. Since no explanation is provided for the use of three moles of glycine to get a 1:1 product it can be assumed that the authors have incorrectly assumed that use of glycine and $MgSO_4$ in 3:1 mole ratio will result in a so-called trisglycine epsomite. However, after measuring the unit cell and finding it in agreement with **2** the authors did not realize that they have obtained a known compound.

Under the heading CHN analysis the authors reported '*The CHN analyser exposes that the title compound contains C=7.05%, H=5.83% N=7.05% and S= 8.71%. using CHNS mode'*. Indeed the analytical data exposes that the title compound is a dubious material due to the disagreement with calculated % of C, H, N and S (Table 1) for the formulae of either **1** or **2**.

Table 1. Calculated elemental analytical data for the formula units of **1** and **2**

Molecular formula	Composition	FW	C	H	*N*	S	Mg	O
$[(Gly)_3MgSO_4(H_2O)_7]$ **1**	$MgC_6H_{29}N_3O_{17}S$	471.76	15.27	6.21	8.91	6.80	5.15	57.66
$[Mg(H_2O)_4(Gly)_2][Mg(H_2O)_6](SO_4)_2$ **2**	$Mg_2C_4H_{30}N_2O_{22}S_2$	571.12	8.41	5.31	4.91	11.23	8.51	61.63

The mismatch of the analytical data despite the identical nature of the unit cell with **2** indicates the possible presence of an impure phase like gamma glycine (due to use of excess reagent) in addition to the known compound **2**. The observation of a second harmonic generation (SHG) efficiency of 0.792 times as that of KDP adds credence to the impurities as gamma glycine is an SHG active solid [4, 5] and centrosymmetric solids do not give any SHG response [6].

Although the authors report IR bands to an accuracy of 0.01 cm^{-1}, some assignments are incorrect and appear questionable. Reliable spectral data for **2** are well documented [3]. It is shown that the crystal obtained is not any new material but a known compound **2** containing impurities. Hence the spectral data and optical studies of such a material are meaningless and do not deserve any further discussion.

Of the amino acid based materials reported in the literature, a large number of dubious crystals [4-7] are based on glycine and several were first listed in a case study [5]. Trisglycine epsomite is a new entrant to this list.

In this comment, I have shown the importance of identifying compounds especially new materials by a proper molecular formula in the abstract of a paper and not just by a name abbreviated by a code as in the title paper. In addition, it is important not to use new and incorrect names for example trisglycine epsomite for a known compound viz. tetraaqua-diglycinemagnesium(II) hexaaquamagnesium(II) bis(sulfate). I hope that this comment will be useful to authors (especially to reviewers) to avoid publication of papers on 'new' materials without a chemical formula.

References

1] K. Amudha, P.S. Latha Mageshwari, R. Mohan Kumar, P.R. Umarani, Selective enhancement of second and third-order nonlinear optical properties of newly synthesised trisglycine epsomite single crystal, *Materials Letters* **223** (2018) 33-36. https://doi.org/10.1016/j.matlet.2018.03.165

2] K. Elayaraja, S. P. Parthiban, S. Ramalingom, G. Bocelli, S. N. Kalkura, Tetraaquadiglycine-magnesium(II) hexaaquamagnesium(II) bis(sulfate) *Acta Crystallogr*. **E63** (2007) m2901-m2902. https://doi.org/10.1107/S1600536807052890

3] S. Tepavitcharova, D. Rabadjieva, D. Havlíček, I. Němec, P. Vojtíšek, J. Plocek, Z.Koleva, Crystallization and characterization of the compounds $Gly{\cdot}MSO_4{\cdot}mH_2O$ ($M = Mg^{2+}$, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}; $m = 0, 3, 5, 6$), *J. Mol. Struc*. **1018**, (2012) 113-121 https://doi.org/10.1016/j.molstruc.2012.02.068

4] M. Fleck, A.M. Petrosyan, *Salts of amino acids: crystallization, structure and properties*. Springer, Dordrecht, 2014.

5] M. Fleck, A.M. Petrosyan, Difficulties in the growth and characterization of non-linear optical materials: a case study of salts of amino acids. *J. Cryst. Growth* **312** (2010) 2284-2290.

6] 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. http://dx.doi.org/10.1080/15421406.2019.1624027

7] B.R. Srinivasan, A.M. Petrosyan, Comment on "A Study on the Growth and Characterization of Zinc Sulphate Mono Hydrate Doped Glycine NLO Single Crystals" *Ferroelectrics* **520** (2017) 274-275 and references therein http://dx.doi.org/10.1080/00150193.2017.1388890

Footnotes

referred to as compound **2** to avoid use of a long name or a big formula