

Comments on the paper: Comparative study of mechanical, dielectric and electrical properties of solution grown semi-organic NLO crystal glycine with additives-ammonium oxalate, potassium and barium nitrate

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A reinvestigation of the growth of the nonlinear optical (NLO) crystal glycine ammonium oxalate is reported. The slow evaporation of an aqueous solution containing equimolar quantities of glycine and ammonium oxalate monohydrate results in the fractional crystallization of ammonium oxalate monohydrate and not the semi-organic nonlinear optical (NLO) crystal glycine ammonium oxalate as reported by the authors of the title paper in *Indian J Pure & Appl Phys*, 51 (2013) 55-59.

Keywords: Glycine, Ammonium oxalate, Glycine ammonium oxalate, Nonlinear optical crystal, Fractional crystallization, Improper characterization

1 Introduction

The growing number of publications on crystals many of which are salts based on amino acids and referred to as 'new nonlinear optical materials', is an indication of the efforts being put by several research groups to discover new nonlinear optical (NLO) materials. In this frontier area of research, it is of concern to note that in addition to several valuable works, crystals which have not been properly characterized are also being published under the name new NLO crystals. Several such erroneous papers were brought to the attention of the scientific community by Fleck and Petrosyan¹ in a case study of salts of amino acids where these authors convincingly proved that many of the so called novel NLO materials, were actually not novel but in fact crystals of the starting amino acid used for crystal growth.

Glycine an achiral amino acid, represented by the zwitter ionic formula ${}^+\text{NH}_3\text{-CH}_2\text{-COO}^-$ exists in three polymorphic modifications namely alpha glycine² (α), beta glycine³ (β) and gamma glycine⁴ (γ). Of these the β - and γ -modifications of glycine crystallize in non-centrosymmetric space groups. A majority of the structurally characterized compounds of glycine with halogen or metal-halogenides in a recent review article of Fleck⁵ are centrosymmetric. In addition to this, several glycine based compounds which were initially reported as novel NLO crystals, were later shown to be improperly characterized and have been

extensively commented^{1,6-16}. In many cases, these so called novel NLO crystals were unambiguously shown to be either the α - or γ - forms of glycine (Table 1). In some cases well-known compounds of glycine were reported under a different name with different composition. In two cases (entry No. 16 and 17 in Table 1) the reported data were not found to be in agreement with the proposed composition. It is unfortunate that the list of improperly characterized NLO crystals based on glycine exceeds a recent list compiled for the improperly characterized L-alanine compounds¹⁷.

The glycine-oxalic acid system has been a subject of recent research and four new structurally characterized compounds are known¹⁸⁻²⁰. In these centrosymmetric crystals, a proton transfer from the oxalic acid to glycine is observed to form a glycinium moiety in the product crystal. The title paper by Ravishankar *et al*²¹, reporting solution growth of a NLO crystal namely glycine ammonium oxalate attracted our attention. As ammonium oxalate does not contain any acidic protons unlike oxalic acid, and all crystals from the glycine-oxalic acid system known so far, are centrosymmetric, the reported claim of growth of an NLO crystal appeared very unusual. In addition, the absence of a proper chemical formula for the so called glycine ammonium oxalate NLO crystal and the non-reporting of any characterization data indicated that the formulation of the said crystal

Table 1 — List of improperly characterized compounds of glycine

No.	so called NLO crystal initially claimed	Actual crystal	Ref.
1	1,3 diglycyl thiourea	α -glycine	1
2	triglycine acetate (TGAc)	α -glycine	1
3	bisglycine hydrogenchloride (BGHC)	γ -glycine	1
4	glycine hydrobromide	diglycine hydrobromide	1
5	diglycine nitrate (DGN)	α -glycine	1
6	$C_2H_{11}NO_9KCl$	γ -glycine	1
7	glycine zinc sulphate (GZS) $Gly \cdot ZnSO_4 \cdot 7H_2O$	$Gly \cdot ZnSO_4 \cdot 5H_2O$	1
8	glycine barium dichloride ($GlyBaCl_2$)	$Gly_2 \cdot BaCl_2 \cdot H_2O$	1
9	tetra glycine barium chloride (TGBC)	$Gly_2 \cdot BaCl_2 \cdot H_2O$	1
10	glycine zinc chloride (GZC)	Diglycine $ZnCl_2$ dihydrate $Gly_2 \cdot ZnCl_2 \cdot 2H_2O$	1
11	glycine lithium chloride (GLC)	γ -glycine	6, 7
12	bis-glycine sodium nitrate (BGSN)	α -glycine	8
13	glycine picrate (GP) $GlyH \cdot C_6H_3N_3O_7$	glycine glycinium picrate $Gly \cdot GlyH \cdot C_6H_3N_3O_7$	9-11
14	$2Gly \cdot HF \cdot HCl$ glycine-chloride-fluoride (GCF)	$2Gly \cdot HCl$	12
15	$2Gly \cdot H_2SO_4 \cdot HNO_3$ α -glycine sulpho-nitrate	$Gly \cdot HNO_3$	12
16	$3Gly \cdot KIO_3$ glycine potassium iodate	Unspecified*	12
17	$3Gly \cdot KNO_3$ glycine potassium nitrate (GPN)	Unspecified*	12
18	glycine sodium-potassium nitrate (GSPN-1) $Gly \cdot NaNO_3 \cdot KNO_3$	γ -glycine	13
19	$6Gly \cdot NaNO_3 \cdot KNO_3 \cdot 2HCl$ (GSPN-2)	γ -glycine	13
20	glycine sodium-barium nitrate $6Gly \cdot NaNO_3 \cdot Ba(NO_3)_2$ (GSB)	γ -glycine	13
21	glycine hydrogen potassium fluoride (GHKF)	γ -glycine	13
22	bis-glycine maleate (BGM)	glycinium hydrogen maleate	14
23	N-acetyl glycine phosphite (AGPI)	glycinium phosphite	15
24	glycine barium nitrate potassium nitrate (GBNPN)	γ -glycine	16
25	glycine ammonium oxalate (GAO)	ammonium oxalate monohydrate	This work

Abbreviations used: Gly = glycine; *Reported data for the NLO crystal not in agreement for proposed composition and structure. For details see¹².

was inappropriate. Hence we have reinvestigated the crystal growth of glycine ammonium oxalate and the results of our study are described in this comment.

2 Experimental Details

Commercially available γ -glycine (Spectrochem), ammonium oxalate monohydrate (Loba Chemie) and double distilled water were used for crystal growth from aqueous solution. Infrared (IR) spectra were recorded in KBr matrix using a Shimadzu (IR Prestige-21) FT-IR spectrometer in the range $4000 - 400 \text{ cm}^{-1}$.

2.1 Reinvestigation of slow evaporation solution growth of glycine ammonium oxalate

A mixture of glycine (0.751 g, 10 mmol) and ammonium oxalate monohydrate (1.421 g, 10 mmol) was taken in 30 ml of double distilled water, stirred well to obtain a clear solution. The reaction mixture was filtered and the clear filtrate was left undisturbed for crystallization. Slow evaporation of solvent maintained at room temperature resulted in the separation of transparent crystals after 3-4 days. The crystals were isolated by filtration, washed with little ice-cold water and dried in air to yield 0.780 g of

crystalline product. The crystals thus obtained are labeled as compound **1** and were analysed by IR spectra and chemical analysis.

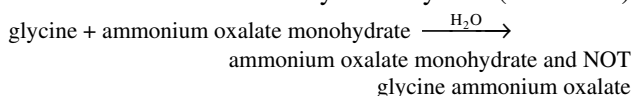
3 Results and Discussion

The authors of the title paper²¹ report to have grown by slow evaporation solution growth technique, single crystals of a nonlinear optical glycine ammonium oxalate from an aqueous solution containing glycine:ammonium oxalate in 1:1 mole ratio (Scheme 1). It is not clear why a crystal from this reaction system is called glycine ammonium oxalate and abbreviated as GAO. Since the authors do not give any molecular formula for their solution grown GAO crystal in the entire paper, it is not clear if the composition of GAO is the same as that of the reagents taken for crystal growth. The statement in the introduction of the title paper '*Studies such as dielectric constant and dielectric loss whose dependence on frequency confirms the grown crystal behaviour and purity*' is unacceptable because dielectric studies cannot be used as a characterization technique to infer the nature and composition of a crystalline compound. Although the authors' write in experimental details '*The crystals were also*

characterized with XRD, FTIR to confirm the crystallinity and presence of additives', no such data were reported anywhere in the entire paper. In view of this, we have reinvestigated the reported work by growing crystals, under the same conditions in the reported paper²¹, so as to unambiguously characterize the product.

The crystalline material obtained by us in the crystal growth reaction is referred to as compound **1**. We have repeated the crystal growth reaction and confirmed that the yield and IR spectrum of compound **1** are highly reproducible. A comparison of the IR spectrum of **1** with that of the starting materials namely glycine and ammonium oxalate monohydrate reveals that the spectrum of **1** is identical to that of pure ammonium oxalate (Fig. 1). The coincidence of the IR spectra clearly shows that no glycine ammonium oxalate crystal as claimed by the authors is formed in the crystal growth reaction. An analysis of the crystal (compound **1**) by spot tests²² reveals that the crystal gives positive test for the presence of both ammonium and oxalate as expected. The ninhydrin test revealed the absence of any primary amino acid (glycine) in the product.

The above observations clearly indicate that there is no chemical reaction between glycine and ammonium oxalate unlike in the glycine-oxalic acid system where products like glycinium oxalate¹⁸, bis(glycinium) oxalate¹⁹, are formed due to proton transfer from oxalic acid to glycine. Since ammonium oxalate does not contain any free acidic protons, no such reaction takes place. Hence, the observation of formation of ammonium oxalate monohydrate crystals (Scheme 1)



Scheme 1

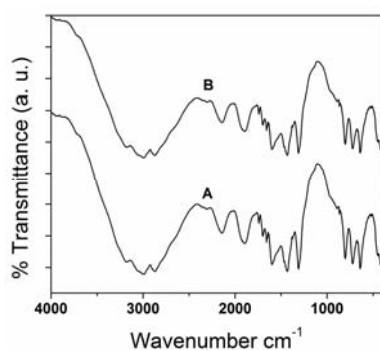


Fig. 1 — Comparative infrared spectra of compound **1** (B) and pure ammonium oxalate monohydrate (A)

in the crystal growth reaction is not at all surprising and can be correctly explained due to the fractional crystallization of ammonium oxalate monohydrate. Both reactants are water soluble and the less soluble ammonium oxalate monohydrate (1.0 g/20 ml) crystallizes first. The more soluble glycine (5.0 g/20 ml) remains in solution. Since ammonium oxalate monohydrate crystallizes in the orthorhombic non-centrosymmetric $P2_12_12$ space group²³, its formation can also explain the observed SHG characteristics for the glycine ammonium oxalate crystal which is actually ammonium oxalate monohydrate. In the title paper, the authors have claimed the growth of another NLO crystal namely glycine barium nitrate potassium nitrate, from an aqueous solution containing glycine:barium nitrate:potassium nitrate in 1:¼:¾ mole ratio. Unfortunately, this crystal has also been wrongly formulated¹⁶ as it can easily be proved to be γ -glycine based on a comparison of its unit cell data reported by the same authors²⁴ with that of γ -glycine⁴. Here again the product crystal formed can be explained due to the fractional crystallization of γ -glycine.

4 Conclusions

The main findings of the present work are as follows: (i) Any crystalline material should be represented by a proper chemical formula and not by an arbitrary name. (ii) In a crystal growth study, the formation of a product crystal depends on the reactivity characteristics of the reagents used for crystal growth. (iii) New compounds/crystals cannot be formulated by disregarding the chemistry of the reactants and based on an assumption that a crystal grown from a mixture of precursor materials (for example glycine and ammonium oxalate) taken in a preferred ratio necessarily represents an expected compound namely glycine ammonium oxalate. Such a procedure is an unscientific method of product characterization and leads to erroneous conclusions as has been proved for the glycine ammonium oxalate crystal. (iv) The chemical composition of a product crystal should be proved by acceptable scientific methods of characterization preferably by single crystal X-ray diffraction when crystals are available. (v) Infrared spectroscopy is one useful method to distinguish products from the reagents as has been shown in the case of the so called NLO crystal glycine ammonium oxalate. (vi) Unlike oxalic acid, ammonium oxalate exhibits no reactivity towards glycine due to which the slow evaporation of an aqueous solution containing equimolar quantities of

glycine and ammonium oxalate monohydrate results in the fractional crystallization of ammonium oxalate monohydrate and not the semi-organic NLO crystal glycine ammonium oxalate. (vii) Studies of dielectric properties, electrical properties and mechanical properties of a crystalline compound are meaningless without unambiguously establishing the correct identity (formula) of a crystalline material under study.

In view of the improper characterization of the glycine ammonium oxalate crystal and glycine barium nitrate potassium nitrate crystal which are ammonium oxalate monohydrate and gamma glycine, respectively, the title paper reporting solution growth of such crystals is completely erroneous.

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