

Can a ‘magnesium sulfate admixed *L*-threonine’ crystal be grown by slow evaporation solution growth method?

Bikshandarkoil R. Srinivasan

Department of Chemistry, Goa University, Goa 403206, INDIA

Email: srini@unigoa.ac.in Telephone: 0091-(0)832-6519316; Fax: 0091-(0)832-2451184

Abstract

Slow evaporation of an aqueous solution containing *L*-threonine and magnesium sulphate heptahydrate, results in the fractional crystallization of the less soluble *L*-threonine crystal and not any novel optoelectronic ‘magnesium sulfate admixed *L*-threonine’ crystal as reported by Pahal Raj et al in Optik, 124 (2013) 6887-6891.

Keywords: *L*-threonine; magnesium sulfate heptahydrate; optoelectronic material; MgSQ admixed *L*-threonine; improper characterization.

1. Introduction

The synthesis, characterization and crystal growth of compounds crystallizing in non-centrosymmetric space groups is a frontier area of research, in view of the possible applications of such crystals for nonlinear optical (NLO) activity. For growth of new NLO crystals, the readily available *L*-amino acids are often employed as reagents and reacted with other reagents for example metal salts, with the expectation that the chirality of the amino acid will be transferred to a new product crystal containing the metal. While many reactions do result in the formation of a new product crystal different from the starting materials, in some cases no new product is formed, resulting in the fractional crystallization of the less soluble amino acid. Such a product crystal can still exhibit NLO property due to the chiral nature of the amino acid. Unfortunately some researchers overlook this aspect and report a known amino acid under different names for example novel NLO crystal, semiorganic NLO

crystal, novel optoelectronic material etc. Several such erroneous papers were brought to the attention of the scientific community by Fleck and Petrosyan in a case study of salts of amino acids [1]. In this case study, these authors have analyzed the several difficulties in crystal growth and characterization of NLO materials and showed that many of the erroneous publications are a result of incorrect interpretation of the unit cell parameters and spectral data. In addition, Fleck and Petrosyan 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. In spite of publication of this case study, more cases of erroneous reports continue to appear in the literature in the area of crystal growth of NLO materials and have been extensively commented [2-15]. The recent paper by Puhaj Raj *et al* [16] entitled, ‘*Structural, optical and mechanical property analysis of magnesium sulphate admixed L-Threonine: A novel optoelectronic material*’, is one such erroneous paper reporting the growth of the well-known L-threonine crystal under the name viz. ‘magnesium sulphate admixed L-threonine’ as will be shown in the following comment.

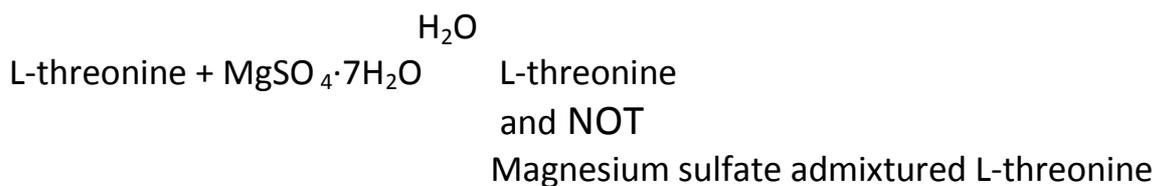
2. Can a ‘magnesium sulfate admixed L-threonine’ crystal be actually grown?

The authors of [16] report to have grown by slow evaporation of an aqueous solution containing L-threonine and magnesium sulfate heptahydrate, a so called ‘magnesium sulphate admixed L-threonine’ (1) crystal. It is not clear why the authors gave an unusual name for their crystal abbreviated by a code LTMS instead of a proper chemical formula. No formula is given in the entire paper. It is not possible to comprehend, if the term ‘magnesium sulphate admixed L-threonine’ actually refers to a Mg(II) complex of L-threonine or to something else. It is also not clear why the authors chose this name (indicating that the crystal is anhydrous) for 1 in contrast to the result of their thermal study where the authors claimed the following: ‘*Initial weight loss (2%) is observed near the temperature 80 °C corresponding to the liberation of water molecule of magnesium sulphate heptahydrate, which is indicated in*

the DTA curve by a endothermic peak'. The commented paper has several more questionable statements some of which are given below:

i) Additional reflections were seen and it indicates the presence of Magnesium Sulphate crystallites within the mixed crystals which is identified by comparing with powder diffraction pattern of pure L-Threonine. ii) From the comparison of pure L-Threonine, δ values are shifted to downward for LTMS crystal. This may be attributed to shielding effect of $MgSO_4$ on L-Threonine. iii) From the thermal studies, it is observed that melting point of grown crystal has been increased when compared to that of pure L-Threonine and may be due to the incorporation of $MgSO_4$ strengthens bonds within the crystal.

The above unscientific claims clearly indicate that the research reported by Puhaj Raj *et al* [16] is dubious, and necessitates a reinvestigation of the reported work to settle the exact nature of the product. However, from the reported synthetic details of the authors mentioning 'L-threonine and magnesium sulphate heptahydrate were taken in 1:0.5' it is not possible to make out if the 1:0.5 corresponds to ratio in terms of weight or moles. In view of this, both reactions were performed. Crystals isolated from reactions using 1:0.5 by weight as well as mole ratios (Scheme 1) turned out to be pure L-threonine (~75% yield) as evidenced by a coincidence of their IR spectra with that of pure L-threonine [8]. The product formation can be explained due to no chemical reaction between the reagents and fractional crystallization of the less soluble L-threonine [17]. The more soluble $MgSO_4 \cdot 7H_2O$ remains in solution.



Scheme 1

An IR spectral proof was recently used by Petrosyan *et al* [8] to prove that a so called *L*-threonine formate crystal is actually *L*-threonine. In order to prove the absence of Mg(II) as well as sulfate in the grown crystals, simple chemical tests [18] for these species were performed, which as expected turned out to be negative confirming that the product crystal is pure *L*-threonine. The formation of only *L*-threonine can also be evidenced from the reported IR spectrum of these authors which is identical to that of *L*-threonine [8]. It is well documented that the tetrahedral sulfate ion exhibits four characteristic vibrations (ν_1 , ν_2 , ν_3 and ν_4) all of which are Raman active and only two are IR active. The IR active asymmetric stretching vibration (ν_3) occurs as an intense signal at 1105 cm^{-1} [19]. Instead of locating and assigning this band, the authors interpreted their IR spectrum by incorrectly assigning a very weak signal at 444 cm^{-1} for the stretching vibration of the sulfate. In view of some vibrations of *L*-threonine also occurring in the sulfate region, the presence of sulfate should be doubly checked by locating the IR inactive symmetric stretching vibration (ν_1) which occurs as an intense signal in the Raman spectrum at 983 cm^{-1} [19] but no such exercise was done.

The situation observed in this so called ‘magnesium sulphate admixed *L*-threonine’ system is very similar to the case of another so called ‘*L*-valine zinc sulfate’ crystal, which is actually *L*-valine [20]. Incidentally the same research group (Puhaj Raj & Ramachandra Raja) had also reported *L*-valine under the name ‘*L*-valine zinc sulfate’ crystal. Since several instances of isolation and reporting of known amino acids under the name novel NLO crystal are well documented in the literature in the form of critical comments [1-8, 11-12, 15, 20-23], the report on *L*-threonine crystal with the name ‘magnesium sulfate admixed *L*-threonine’ [16] is not very surprising. It is only unfortunate that the authors of the commented paper [16] could find MgSO_4 in crystals of *L*-threonine as evidenced by their claim, *The presence of MgSO₄ in LTMS is confirmed from the EDAX spectrum*. The presence of Mg in their sample

is only an impurity and can be explained by the synthetic protocol used by these authors for crystal growth which is supposed to be as follows: *The solution was allowed to evaporate slowly until the solvent was completely dried. The purity of the synthesized salt was further increased by successive recrystallization process.* Due to complete evaporation of the solvent the authors initially obtained the entire starting materials back. The samples used for EDAX, X-ray powder pattern, thermal study etc. were *L*-threonine crystals contaminated with the Mg(II) salt, before the successive recrystallization of the original mixture had resulted in the formation of pure *L*-threonine crystals. An intermediate batch of impure crystals and not the final pure *L*-threonine material was used for some of the characterization. Thus the synthetic protocol and the incorrect choice of crystals employed by the authors for the characterization, can explain the additional lines in the powder pattern, presence of Mg in the EDAX study, and a small amount of water loss in thermal study etc. In earlier report [15] it has been shown that mere observation of the presence of a few elements in an EDAX study is no valid proof for product formation. The commented paper is another example showing an improper use of EDAX study for product characterization.

4. Conclusions

In summary, it is proved that at room temperature, slow evaporation of an aqueous solution containing *L*-threonine and magnesium sulphate heptahydrate in 1:0.5 mole ratio, results in the fractional crystallization of the less soluble *L*-threonine crystal and not any so called ‘magnesium sulfate admixed *L*-threonine’ crystal.

Footnotes:

To avoid use of non-standard abbreviations the crystal is identified as compound 1.

References:

- [1] 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.
- [2] Z. Tylczyński, M. Wiesner, Comment on “Ferroelectricity in glycine picrate: An astonishing observation in a centrosymmetric crystal” [*Appl. Phys. Lett.* 95, 252902 (2009)], *Appl. Phys. Lett.* 96 (2010) 126101.
- [3] V.V. Ghazaryan, M. Fleck, A.M. Petrosyan, Glycine glycinium picrate—Reinvestigation of the structure and vibrational spectra, *Spectrochim. Acta A78* (2011) 128–132.
- [4] A.M. Petrosyan, V.V. Ghazaryan, M. Fleck, Comments on the papers recently published by M.M. Khandpekar and S.P. Pati, *J. Cryst. Growth* 322 (2011) 117–118.
- [5] A.M. Petrosyan, V.V. Ghazaryan, M. Fleck, Comments on the papers recently published by M.M. Khandpekar et al., *Opt. Commun.* 284 (2011) 4295–4296.
- [6] A.M. Petrosyan, V.V. Ghazaryan, M. Fleck, On the existence of “bis-glycine maleate” *J. Cryst. Growth* 359 (2012) 129–131.
- [7] J. Baran, A. M. Petrosyan, Comments on the Paper by R. Ezhil Vizhi et al. “Synthesis, Crystal Growth, Structural, Dielectric and Ferroelectric Properties of N-Acetyl Glycine Phosphite (AGPI) Single Crystals, *Ferroelectrics*, 432 (2012) 117–118.
- [8] A.M. Petrosyan, V.V. Ghazaryan, M. Fleck, On the existence of “*L*-threonine formate”, “*L*-alanine lithium chloride” and “bis *L*-alanine lithium chloride” crystals, *Spectrochim. Acta* 105A (2013) 623–625.
- [9] B.R. Srinivasan, K.R. Priolkar, Comment on ‘Synthesis, growth, structural, spectroscopic, crystalline perfection, second harmonic generation (SHG) and thermal studies of 2-aminopyridinium picrate (2APP): A new nonlinear optical material’ [*Solid State Sci.* 14 (2012) 773–776], *Solid State Sciences* 20 (2013) 15–16.
- [10] B.R. Srinivasan, Z. Tylczyński, V.S. Nadkarni, Comment on ‘Synthesis, growth, structural, spectral, linear and nonlinear optical and mechanical studies of a novel organic NLO single crystal 4-Bromo 4-Nitrostilbene (BONS) for nonlinear optical applications’ *Opt. Mater.* 35 (2013) 1616–1618.
- [11] B.R. Srinivasan, K.T. Dhavskar, 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, *Indian J. Pure & App Phy* 52 (2014) 60–63.
- [12] B.R. Srinivasan, On the existence of *L*-proline cadmium bromide, *Spectrochim. Acta* 116A (2013) 639–641.

Manuscript Ref. No 13-1903

- [13] B.R. Srinivasan, P. Raghavaiah, V.S. Nadkarni, Reinvestigation of growth of urea thiosemicarbazone monohydrate crystal, *Spectrochim. Acta A112* (2013) 84-89.
- [14] B.R. Srinivasan, T.A. Naik, Z. Tylczyński, K.R. Priolkar, Reinvestigation of growth of thiourea urea zinc sulfate crystal, *Spectrochim. Acta 117A* (2014) 805-809.
- [15] B.R. Srinivasan, Can zinc(II) ions be doped into the crystal structure of *L*-proline cadmium chloride monohydrate crystal?, *Spectrochim. Acta 116A* 635-638 (2013).
- [16] A. Puhaj Raj, I. J. D. Ebenezer, C. Ramachandra Raja, Structural, optical and Mechanical property analysis of magnesium sulphate admixed *L*-Threonine: A novel optoelectronic material, *Optik*, 124 (2013) 6887-6891.
- [17] Merck Index, Ninth Edition, Published by Merck & Co. Rahway, New Jersey 1976.
- [18] G. Svehla, Vogel's Qualitative Inorganic Analysis, Pearson, Seventh Edition (2011).
- [19] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, John Wiley & Sons, New Jersey, Sixth Edition, 2009.
- [20] B.R. Srinivasan, R.N. Jyai, Reinvestigation of growth *L*-valine zinc sulfate crystal, *Spectrochim. Acta*, A120 (2014) 621-624.
- [21] B.R. Srinivasan, On the existence of 'glycine barium nitrate potassium nitrate' crystal, *Optik* 125 (2014) 3606-3607.
- [22] B.R. Srinivasan, On the existence of '*L*-asparagine cadmium chloride monohydrate' crystal, *Optik* 125 (2014) 2927-2929.
- [23] B.R. Srinivasan, Comments on the paper: 'Studies on structural, thermal and optical properties of novel NLO crystal bis *L*-glutamine sodium nitrate', *Materials Letters* 131 (2014) 373-374.