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LETTER TO THE EDITORS

CRYSTALLIZATION OF GLYCINE–SULFATE

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TGS and DGS crystals have been grown from the aqueous solutions and the results are reported in this paper. It has been found that the pH of the solution at the time of crystallization is the most important parameter determining the crystallization of the different glycine–sulfate compounds. It has been shown that for the crystallization of TGS the required pH is ≥ 1.5.

The most well known glycine–sulfate compound is triglycine sulfate (TGS). It exhibits ferroelectric properties at room temperature and has a variety of applications in technology [1–3]. Anhydrous diglycine sulfate compound. DGS is a non-ferroelectric orthorhombic crystal [4,9]. After the discovery of the ferroelectric activity of TGS in 1956 by Matthias et al. [5], many workers have grown single crystals of TGS [6–8]. However, recent reports on the growth of glycine–sulfate compounds show controversy regarding the required growth conditions for these crystals [4,9–11]. The present authors have systematically studied the growth of TGS and DGS crystals from aqueous solutions and the results are reported in this paper. An attempt has been made to establish the required conditions for the growth of TGS and DGS crystals and it has been shown that the pH of the solutions (and not the molarity ratio of the reacting solutions) at the time of crystallization is the most important parameter deciding the growth of the crystals.

Most of the research workers [12–14] have grown TGS crystals from aqueous solutions of glycine and sulfuric acid taken in stoichiometric molar ratios. Whipps et al. [9] and Wood and Holden [4] have reported that when proportions of amino acid and sulfuric acid are taken in equal molar ratio, they obtained DGS crystals. Contrary to this, Dominquez et al. [10] have reported that when glycine and sulfuric acid are taken in equal molar ratios TGS crystals are obtained. In addition to this, they have shown that molar proportions of sulfuric acid and glycine of 1 : 2 and 1 : 3 also give TGS crystals. They have further reported that the solutions having pH > 1.9 give TGS crystals and, if the pH is between 1 and 1.9, non-TGS crystals are obtained, i.e. diglycine sulfate anhydrous or diglycine sulfate monohydrated. On the other hand Szczepanska [11] has reported that for the growth of TGS crystals the optimum pH of the solution should be 1.5.

Since the pH of the saturated solution, besides varying with the proportions of reacting solutions, also varies with the temperature at which the solution is saturated, these controversial results pose the question: Do saturated solutions of glycine and sulfuric acid when taken in 3 : 1 molar ratio always have the required pH for the crystallization of TGS? Table 1 gives the conditions for the growth of TGS and DGS crystals as reported by various workers. From the table it is evident that the required growth conditions are not conclusive. There is a controversy over the required pH for the growth of particular crystals. From the information on hand it is not known whether it is the proportions of glycine and sulfuric acid or whether it is the pH of the solution that determines the crystallization of a particular compound.

In the present study a number of aqueous solutions with various proportions of glycine and sulfuric acid were taken. The pH of these solutions were measured when saturated at room temperature (28°C). In each case seeds were obtained by free evaporation at

Table 1
Conditions for the growth of TGS and DGS crystals as reported by various workers

Authors	Growth conditions for TGS crystals	Growth conditions for DGS crystals
Whipps et al. [9]	Proportions of amino acid to sulfuric acid of 2 : 1 and 3 : 1 always give TGS crystals	Proportions of amino acid to sulfuric acid of 1 : 1 give DGS crystals
Wood and Holden [4]		Solution containing glycine and sulfuric acid in equal molar proportions gives DGS crystals
Dominquez et al. [10]	Solutions containing sulfuric acid and glycine in the proportions of 1 : 1, 1 : 2 and 1 : 3 give TGS crystals; when the pH of the solution is >1.9, it gives TGS crystals	If the pH of the solution is between 1 and 1.9, it gives non-TGS crystals
Szczepanska [11]	For TGS crystals optimum pH required is 1.5	Solutions having pH < 1 give monohydrated diglycine sulfate crystals; at a very low pH, DGS crystals are obtained

the constant room temperature and were planted in the respective solutions. Crystals growth was carried out at the same constant temperature. It was found that the morphology of the crystals varied with the pH of the solutions. Two different types of crystal were found to crystallize, which were identified as TGS and DGS crystals. The crystals were identified as monoclinic and orthorhombic from the crystal morphology, which was confirmed by X-ray analysis. Chemical analysis of the crystals confirmed this identification. The results were also supported by observing the phase transition, the hysteries loop and the domains of the TGS crystals. The results obtained for solutions of different pH are given in table 2.

From the results obtained it may be concluded that:

(i) The pH of the solution is an important criterion for the crystallization of glycine–sulfate compounds.

Table 2
Conditions for the growth of TGS and DGS crystals as observed by the present authors

pH of the saturated solution at 28°C	Molar ratio of glycine and sulfuric acid	Triglycine sulfate crystals obtained (TGS)	Anhydrous diglycine sulfate crystals obtained (DGS)
0.5	2 : 1	None	All the crystals
1.0	3 : 1	Very few	Most of the crystals
1.25	3 : 0.87	Most of the crystals	A few crystals
1.5	3 : 0.72	All the crystals	None
2.0	3 : 0.58	All the crystals	None
2.5	3 : 0.43	All the crystals	None

The type of the compound crystallizing depends on the actual pH of the solution at the time of crystallization.

(ii) Solutions having $1.0 \geqslant pH \geqslant 0.5$ always give DGS crystals.

(iii) Solutions having $1.25 \geqslant pH \geqslant 1.0$ give either TGS or DGS crystals. Within this pH range the number of TGS crystals increases with pH. At pH = 1.3, most of the crystals obtained are TGS; however, a few DGS crystals are obtained.

(iv) Solutions having $2.5 \geqslant pH \geqslant 1.5$ always give TGS crystals.

(v) For the crystallization of TGS crystals, $1.8 \geqslant pH \geqslant 1.5$ is ideal since at higher pH the solution is unstable.

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