

Growth of Pure and Doped Triglycine Sulphate Single Crystals

Mohamed A. Gaffar¹ and Abd El Aziz A.F. Abd El Aziz

*Physics Department, Faculty of Science, Assiut University,
Assiut, Egypt.*

ABSTRACT. Large single crystals of pure and doped Triglycine sulphate are obtained in the temperature range 44 to 28°C using the falling temperature technique. The divalent ions Ni²⁺, Co²⁺ and Cu²⁺ as well as the trivalent Cr³⁺ and Fe³⁺ are used as the dopant ions. The effect of these ions upon the speed of growth, crystal parameters, density, crystal morphology, surface relief, colour and crystal purity is presented. The variation in the measured physical properties is strongly dependent on the complexes formed by the dopants.

Single crystals of triglycine sulphate (NH₂CH₂COOH)₃.H₂SO₄ (abbreviated as TGS) are applied extensively in pyroelectric detectors. Their modified forms as well as their isomorphs are known to possess the highest pyroelectricity (Schwarz and Poole 1970, and Lock 1971). In many cases, they are the most suitable materials for constructing pyroelectric detectors operating at room temperature. It is also known that TGS has been used as piezoelectric material. The importance of such material for technological applications has carried its growth onto Skylab III (Lal 1981).

The ferroelectric activity of TGS was discovered by Matthias *et al.* (1965). The Curie temperature of TGS lies in the vicinity of 49°C. The phase above the transition has a monoclinic symmetry and belongs to the centrosymmetrical class 2/m. Below the transition temperature, the mirror plane disappears and the crystal belongs to the polar point group 2 of the monoclinic system. Ferroelectricity is found along the direction of the two-fold polar axis (the b-axis) (Wood and Holden 1957, and Hoshino *et al.* 1959).

¹ Present Address: Physics Department, Faculty of Science, Qatar University, P.O. Box 2713, Qattar.

TGS single crystals have been grown by different techniques at room temperature, below the transition temperature, or in the paraelectric phase (Duley and Finnigan 1973, Tsedrik *et al.* 1975, Srivastava and Singh 1976, and Pandya and Vyas 1980). Deviation from stoichiometry not only changes the shape of TGS crystals (Koldovskaya and Gavrilova 1961) but also leads to the crystallization of diglycine sulphate under specific conditions (Whipps *et al.* 1972). The pH value affects considerably the habit of crystals growing from aqueous solution. Tsedrik *et al.* 1975 *e.g.*, studied the effect of the concentration of hydrogen ions on the rate of growth of different faces and the homogeneity of the crystal. Special seed shapes for different crystallographic axes have also been tried (Loiacono and Osborne 1978). The effect of doping such a crystal with mono-, di-, tri-, or tetravalent ions on the kinetics of growth have been also studied by different workers (Toyoda *et al.* 1961, Lielicrap and Wood 1977, and Tsedrik and Kravchenya 1977).

The aim of this article is to report our findings in obtaining large, perfect and homogeneous TGS single crystals. As a first step, a selection of the growth conditions is made to grow pure crystals of TGS. A study of the effect of adding di-, or trivalent ions to the solution (under the same conditions) on the grown crystals is our second goal.

The crystals have been subjected to the measurement of some physical properties including the morphology, density, and X-ray measurement of cell parameters. A detailed study of the physical properties of the grown crystals will follow in another publication.

Experimental

The apparatus and methodology used in the present study are exactly the same as described previously by the authors (Gaffar *et al.* 1980). A decisive factor for growing defect free crystals is to control the conditions of crystallization by taking care of the thermal stability. Crystallization by both continuously slow cooling and by saturated solution techniques have been tried. The continuous slow cooling technique is found to be the most convenient for growing TGS since the rate of evaporation of the solution of TGS at 44°C is relatively high (about 0.06 ml/cm² of the surface area of the solution/day). A period of about 72 hours is spent for insuring thermal stability between the different parts of the crystallizer before adding the solution. The same interval is needed after adding the solution to the seed crystal before beginning the proposed schedule of cooling. During the first week, the temperature is lowered at the rate of 0.15°C/day. Then, the cooling rate is raised gradually until it reaches its final value of 0.3°C/day. The rate of growth along the c-axis is approximately half that along the b-axis. Generally the rate of growth is about 0.5 mm/day.

The powder of TGS is obtained from the reaction of glycine (PROLABO-99.7%) with sulphuric acid in a 3 to 1 molar ratio. The formed powder is redissolved in distilled water, filtered and then dried. This process is repeated two or three times to insure high purity.

As a seed, natural crystals of about 3-4 mm each edge with well developed faces are used. Several TGS seed crystals are obtained by decanting about 200 ml of saturated solution of TGS at $\sim 35^{\circ}\text{C}$ into a small beaker which then is left to cool slowly to room temperature. After several days, some small crystals of well defined edges 2-3 mm each side can be obtained. The choice of the seed is one of the most important factors controlling the homogeneity of the growth. A seed with a cut made along a particular axis is found to be a failure as it is a source of additional nucleation in the solution. Thus, we chose "as grown" small crystals in platelet form, with about 16 mm^2 in cross section and 3-4 mm in thickness, as our initial seed. The most developed faces of the seed are clearly (001) and (110) while the (010) face is almost missing.

The seed crystal is cemented on a teflon platform using special adhesive. Simultaneous growth of more than one crystal is possible. The temperature is controlled to an accuracy of $\pm 0.05^{\circ}\text{C}$. All our crystals are grown in the ferroelectric phase at about 44°C . The pH value of the solution is adjusted around 3.6.

Two groups of ions are chosen to be the dopants in the present study. The first group consists of the divalent ions Ni^{2+} , Co^{2+} or Cu^{2+} . The second group contains the two trivalent ions Cr^{3+} or Fe^{3+} . The salts used are in the form of sulphates (PROLABO 99%). The concentration of the dopant in the growth solution is 1%. We also report trial experiments with 2,3 and 5% in the case of Cr^{3+} .

Excluding the case of Cr^{3+} ions, the addition of impurities decreases the rate of crystallization especially for Co^{2+} and Cu^{2+} . An odd behaviour is found while growing Cr^{3+} doped TGS crystals. The addition of Cr^{3+} in the concentration of 1% changed the regime of crystallization owing to the high chemical activity of these ions. At a concentration of about 3% it is very difficult to grow monocrystals as the rate of crystallization becomes very fast even without lowering the temperature (caused by temperature fluctuations). When the concentration of Cr^{3+} reached 5% we were not able to grow monocrystals. Other dopants do not change the regime of crystallization as much as in the case of Cr^{3+} ions. Doped TGS crystals up to about 6 cm^3 have been grown in about five weeks.

The lattice parameters of the grown crystals have been measured using a single crystal diffractometer with 10^{-4} \AA accuracy for the axial lengths and 10^{-2} degree for the angles. The surfaces of the grown crystals are examined using a polarizing

microscope. The concentration of the dopant in the crystal is determined using the microprobe technique.

Results and Discussion

Purity, Habit and Crystal Colour

For undoped TGS, clear transparent crystals with about 40 sq. cm area and 3 cm thickness have been grown in about 8 weeks. They are free from visible inclusions and without any cracking. In most of the crystals, the (010) face was present even if it was absent in the seed. Crystals doped with Cr^{3+} are violet in colour, gradually increasing from light at 1% to dark at 5% doping (polycrystals in such case). Crystals doped with Ni^{2+} are slightly green, while they are blue in the case of Cu^{2+} , yellow-brownish for Fe^{3+} and pink for Co^{2+} . All crystals are transparent in most parts, with some visible strains for crystals doped with Cr^{3+} owing to the high rate of crystallization, see Fig. 1.



Fig. 1-a. 1. Pure TGS
2. TGS + Cr^{3+}
3. TGS + Ni^{2+}
4. TGS + Cu^{2+}
5. TGS + Co^{2+}
6. TGS + Fe^{3+}

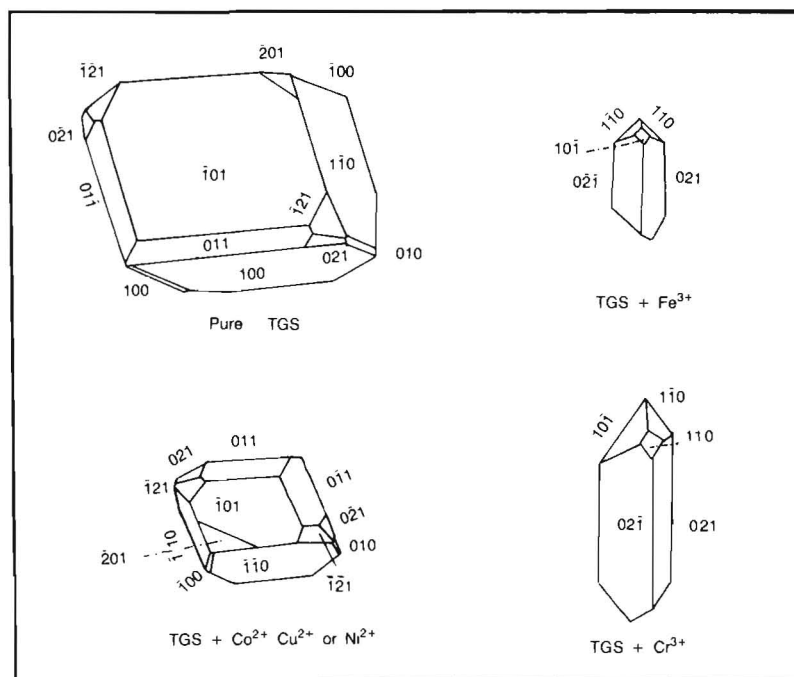


Fig. 1-b. Habit of TGS pure and doped crystals with di- or trivalent ions.

In solutions of TGS containing di- or trivalent ions, metal-glycine complexes are formed and enter the crystal lattice during the growth process. The formation of glycine-copper complexes has been studied by Lösche and Windsch (1965) applying EPR. Taurel *et al.* (1958) using NMR found the concentration of glycine copper complexes to be proportional to the pH value of the solution. Stankowski (1968) reported that Cu^{2+} ions form two magnetically equivalent planar complexes with molecular glycine groups II and III in TGS. These complexes are differently oriented with respect to the b-axis of the crystal. On the other hand Cr^{+3} forms two groups of magnetically equivalent octahedral complexes with glycines II and III and sulphate ions (Waplak and Stankowski 1969). These complexes are differently oriented with respect to the crystallographic axes. The change in shape of the doped crystal is due to a change in the dynamical growth properties. The dynamical equilibrium between dissolution and growth of the various crystal planes is modified in comparison to the equilibrium for pure crystals at the same degree of supersaturation. This is a result of directionally selective "building in" of the complexes from the solution into the crystal.

For the Co^{2+} , Cu^{2+} and Ni^{2+} ions forming planar complexes, the shape of the crystal is slightly modified and the rate of growth remains practically unchanged. However, crystals containing Cr^{3+} or Fe^{3+} changed drastically as a result of the formation of octahedron-shaped complexes. The growth process leads to shapes elongated in the direction of the a-axis. Figure 2 shows the change in shape of TGS crystals doped with Cr^{3+} at different concentrations.

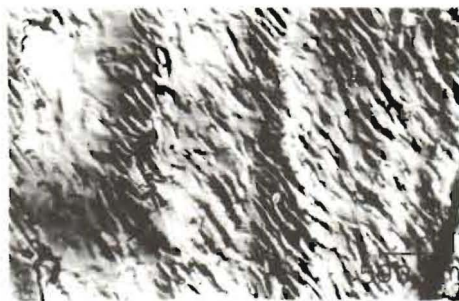


Fig. 2. 1. TGS + 1% Cr^{3+}
2. TGS + 3% Cr^{3+}
3. TGS + 2% Cr^{3+}

Dislocation, Domain Configuration and Dopant Concentration

Figure 3 shows microphotographs of the surface relief of ~ 2 mm thick cleaved plates of pure TGS single crystals as well as doped ones etched with water. From the figure, the etch pits corresponding to the dislocations, which are linear defects, are clearly visible. Obviously, the surface relief is strongly dependent on the type of ion involved. The general structure illustrates the existence of antiparallel domain configurations but the size of such domains differs from one sample to another.

One can notice that the sample containing Ni^{2+} is either a single domain or, at least, it contains less domains in comparison not only with the doped samples, but also with the pure ones.



Pure sample

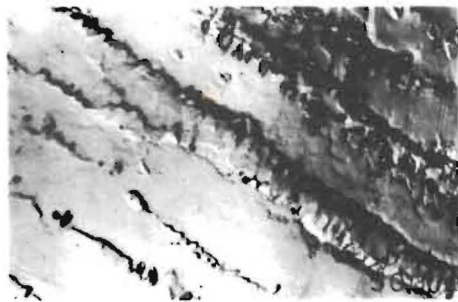
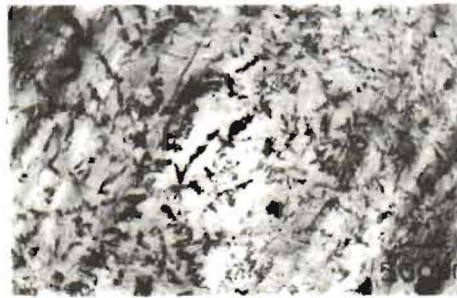
 Ni^{2+} doped sample Co^{2+} doped sample Cu^{2+} doped sample Cr^{3+} doped sample Fe^{3+} doped sample

Fig. 3. Surface morphology of TGS pure as well as samples doped with di- and trivalent ions $\times 1720$.

We examined also the concentration of the impurity ions and their distribution in the crystal with the microprobe technique, and concluded that the distribution of ions in the crystals is not homogeneous. Within the experimental error of the technique, the concentration for all crystals grown from solutions containing 1% additive is about 200 ± 20 ppm (mean value). For crystals containing 2, 3% Cr^{3+} the values are 280 ± 20 ppm, 320 ± 20 ppm, respectively.

Lattice Parameters and Density

The lattice parameters of pure and doped TGS crystals shown in Table 1 are in good agreement with the literature (Wood and Holden 1957). Generally, the maximum variation in the parameters is observed in the crystals containing Ni^{2+} ions, as is also concluded from the physical properties measured for these crystals.

The density of the grown crystals, determined at room temperature by the hydrostatic weighing in toluene with an accuracy of 10^{-3} is given in Table 1. The results show complete coincidence with the literature (Wood and Holden 1957), and the variations in the densities for the doped crystals indicate that the impurity ions enter the lattice in interstitial positions. The concentration of the ions in the crystal depends not only on the ionic radii and the atomic weight of the dopant, but also on the valency and chemical activity of the ions. The calculated and measured densities, shown in Table 1, are in good agreement indicating that the grown crystals are free from inclusions.

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Table 1. Lattice parameters and density of pure and doped TGS single crystals.

| Sample | Ionic radii of the dopant (Å) | Atomic weight of the dopant | a(Å) ± 0.001 | b(Å) ± 0.001 | c(Å) ± 0.001 | β° ± 0.001 | V(Å) ± 0.01 | Density | |
|------------------------|-------------------------------------|--------------------------------------|-----------------|-----------------|-----------------|--------------------------|----------------|---------------------|-----------------------|
| | | | | | | | | measured ± 0.001 | Calculated ± 0.001 |
| Pure TGS | – | – | 9.167 | 12.640 | 5.729 | 105.58 | 639.49 | 1.639 | 1.679 |
| TGS + Ni ²⁺ | 0.69 | 58.69 | 9.132 | 12.634 | 5.727 | 105.97 | 635.25 | 1.691 | 1.690 |
| TGS + Co ²⁺ | 0.72 | 58.44 | 9.162 | 12.642 | 5.717 | 105.60 | 637.74 | 1.674 | 1.683 |
| TGS + Cu ²⁺ | 0.72 | 63.57 | 9.174 | 12.638 | 5.714 | 105.72 | 637.63 | 1.685 | 1.684 |
| TGS + Cr ³⁺ | 0.63 | 52.01 | 9.182 | 12.638 | 5.727 | 105.82 | 639.40 | 1.672 | 1.679 |
| TGS + Fe ³⁺ | 0.64 | 55.85 | 9.171 | 12.633 | 5.723 | 105.59 | 638.69 | 1.698 | 1.681 |

إنماء بلورات كبريتات ثلاثي الجليسين نقية وأخرى مطعمة بالشوائب

محمد عبدالعزيز جعفر^١ و عبدالعزيز أبو الفضل عبدالعزيز

قسم الطبيعة - كلية العلوم - جامعة أسيوط - أسيوط - مصر

من المعروف أن لبلورات ثلاثي جليسين الكبريت تطبيقات تقانية متعددة خصوصاً في مجال الكواشف الكهحرارية، وتتميز دون غيرها في هذا المجال بإمكانية استخدامها عند درجة حرارة الغرفة. ويميز هذه البلورات أيضاً معامل كهربية ضغطية مرتفع، ولأهميتها فلقد كانت هي النموذج الذي وقع عليه الاختيار لمحاولة إنمائها في صورة عالية النقاء في ظهر معامل الأبحاث التي تطلق إلى الفضاء الخارجي.

تمت في هذا البحث محاولات لإنماء هذه البلورات بأبعاد مناسبة وعلى درجة عالية من النقاء، وأستخدم في هذا طريقنا الإنماء المعروفتان، وهما طريقة التخفيض المستمر لدرجة الحرارة، وطريقة سحب الماء المتبخر للحفاظ على محلول النمو عند حالة فوق التشبع. وُجد أن الطريقة الأولى هي الأنسب، وكانت درجة حرارة بداية النمو 44°C ، وهي أقل من درجة حرارة الانتقال الطوري. كان معدل تخفيض درجة الحرارة في البداية هو 15°C ، في اليوم، وفي نهاية عملية الإنماء وصل معدل التخفيض إلى 30°C ، في اليوم، وقد تم الحصول على البلورات بعد حوالي خمسة أسابيع من عملية الإنماء.

وللحصول على محلول النمو أستخدم الجليسين وحامض الكبريتيك بنسبة ٣ إلى ١ مول، حيث المواد الداخلة في التفاعل نقية كيميائياً. بعد الترشيح والتجفيف، يذاب الملح المتكون في ماء مقطر، وتكرر العملية عدة مرات بهدف الحصول على محلول نمو على درجة عالية من النقاء.

كان لنوعية جنين النمو أثر في عملية الإنماء، فلقد لوحظ أن الجنين المقطوع في إتجاه بلوري خاص لا ينمو في صورة بلورة وحيدة، في حين أن الجنين الطبيعي

(١) العنوان الحالي: قسم الفيزياء - كلية العلوم - جامعة قطر - الدوحة - قطر.

المأخوذ من عملية إنماء سابقة ينمو بصورة جيدة. بالإضافة إلى إنماء بلورات نقية أجريت محاولات لدراسة تأثير إضافة بعض العناصر بنسب صغيرة تتراوح ما بين ١٪ و ٥٪ إلى محلول النمو على عملية الإنماء ذاتها، وعلى الخواص التركيبية والطبيعية لهذه البلورات. اخترنا هذه الشوائب لكي يكون بعضها ثنائي التكافؤ (نيكل ونحاس وكوبلت) والبعض الآخر ثلاثي التكافؤ (كروم وحديد).

أجريت دراسة لمعرفة كمية الشوائب التي أمكن لها الوصول إلى داخل الشبكية البلورية للبلورات المنماة باستخدام طريقة المجس الإلكتروني وبحساسية تصل إلى ٢٠٠ جزء بالمليون، كما قيست ثوابت الخلية الأصلية باستخدام مقياس حيود بلورات وحيدة بحساسية تصل إلى 10^{-4} في حالة قياس الأطوال، 10^{-2} في حالة قياس الزوايا. تمت أيضاً دراسة سطح عينات من البلورات المنماة باستخدام مجهر مستقطب الضوء.

تم التوصل إلى أن لون البلورات ودرجة نقائها والمستويات البلورية بها تعتمد كثيراً على وجود أو عدم وجود شوائب في محلول النمو، كما أنها تعتمد على نوعية الأيون المضاف. عندما وصلت نسبة الشوائب في المحلول إلى حد معين، لوحظ عدم نمو البلورات في صورة بلورة وحيدة ولكنها تنمو في صورة متعددة البلورات.