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Synthesis and dielectric studies on pure and doped Triglicine Sulphate single crystals for laser applications

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Amino acids (L-alanine, L- valine , L-histidine) doped Triglycine sulphate(TGS) crystals were grown by solution growth technique. Slow cooling as well as slow evaporation methods were employed to grow these crystals, the concentration of dopants in the mother solution was varied from 0.1 mole% to 10 mole % .The solubility data for all dopant concentrations were determined. The variation in pH and the corresponding habit modification of the grown crystals were characterized with UV - VIS, FT-IR and SHG trace elements and dielectric studies reveal slight distortion of lattice parameter for the heavily doped TGS crystals. The dopants increase the hardness value of the material, which also depends on the concentration of the dopants. Amino acids doping improved the NLO properties. The detailed results on the spectral parameters, habit modifications and constant values will be presented.

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1. Introduction

Triglycine sulphate, abbreviated as TGS, is one of the best ferroelectric materials for device application. This was discovered by Matthias et al (1956). This compound has the most rectangular hysteresis loop and it has high pyroelectric coefficient and low dielectric constant. These properties make it a ferroelectric of great interest. It has a complex chemical and crystallographic structure. It becomes the object of active research for two reasons, firstly, it is one of the very few ferroelectrics known to exhibit a second order phase transition and hence offers possibilities for the observation of genuine critical phenomena very close to the Curie temperature; secondly, it is an order-disorder ferroelectric. These crystals are grown from aqueous solution and are useful in infrared detection due to their interesting physical properties. As a pyroelectric material, TGS possesses an axis of spontaneous electrical polarization along the [010] crystallographic direction which is sensitive to the temperature variation of the TGS single crystals. In recent years, there has been considerable development in infrared detectors, with the aim of achieving the highest performance.

2. Experimental procedure

2.1 Crystal growth

Pure TGS crystals were grown from aqueous solution by slow evaporation and also by slow cooling method (0.5 deg/day). The same method was followed for doped KDP crystals (0.1 mole % L-alanine). The solubility of doped TGS in the solvent was determined for each dopants for temperature 35^0C by dissolving the TGS salt in deionised water in an air-tight container maintained at a constant temperature with continuous stirring. After attaining saturation, the equilibrium concentration of the solute was analysed gravimetrically. The solubility of doped TGS was measured for each dopant and was found to be 32.75grams/100 ml at 40^0 C for L-alanine . The seed crystals were prepared at low temperature by spontaneous nucleation. Seed crystals with perfect shape and free from macro defects were used for growth experiments. Single crystal of TGS and doped TGS were grown using a constant temperature bath (CTB), controlled by the Indtherm temperature programmer/controller. The mother solution was saturated using the initial pH value 4.5 for L-alanine dopant. The growth was carried out for more than 20 days by keeping the bath at a temperature of 40 ^{o}C.

A few nuclei of doped TGS had appeared at the bottom of the beaker and grew for a few days. The change of super saturation was greater than 15% of the critical super saturation during the growth of doped TGS crystals. Constant temperature bath were used for the bulk growth of amino acids doped TGS crystal. Transparent good quality crystals were obtained after 20 days.

2.2 Properties and structure of TGS

The salt, TGS (NH is colourless, odorless and acidic; it is made by reacting a-amino acid with sulphuric acid in the molar ratio of 3:1. Its density is 1.65 - 1.68 g/cm^3.This crystal belongs to the monoclinic system with the space group $P2_1$ number of formula units per unit cell is 2. Wood et al (1957) proposed the parameters of the unit cell as

$a=9.47$ Å, $b=12.69$ Å, $c=5.71$ Å and $\beta=110^0$. Hoshino et al. (1957) chose a different set of axes and determined the lattice parameter to be $a=9.15$ Å, $b=12.69$ Å, $c=5.78$ Å and $\beta=105°$. The polar axis is along the monoclinic (two-fold symmetry) 'b' axis. Above the Curie temperature (T=49°C), the crystal has monoclinic system and belongs to the centro- crystal class $P2_1/m$. So the spontaneous polarization is then lost. Below T_c the mirror plane disappears and the crystal belongs to the polar point group $P2_1$ of monoclinic system. The first detailed investigation of crystal structure was carried out by Hoshino et al (1957) using X-ray diffraction. TGS may be called glycine-di-glycinium sulphate with chemical formula.

$$(NH_3{+}CH_2COO^-)(NH_3^+CH_2COOH)_2\,SO_4^{2-})$$

Of the three glycine groups contained in the asymmetric unit, two assume a completely planar configuration and the third one assumes a partially planar configuration. The bond between two planar groups II and III are responsible for ferroelectric transition. Above the Curie temperature, glycine I molecule is splitted. Reversal of the polarization in the material is largely associated with the rotation of the glycine I group about the crystallographic 'a' axis to change into its mirror image (Whatmore 1986).

In the case of deuterated analogs of TGS, it is not possible to completely replace the hydrogen with deuterium. There are seventeen hydrogen in each TGS molecule. Among the seventeen, eleven are active (64.7%) except the six which are in contact with carbon atom .These eleven active H can be substituted with deuterium by recrystallization (Fang et al 1989a).

Pyroelectric detecting materials possess a number of characteristics which are of significance when considering their use in a given application. They can be used over a large spectral bandwidth, the only requirement being that the energy be absorbed. They can be used over a wide range of temperatures. They have low power requirements and can operate for long period on battery power, and last, but not least, they are generally low-cost devices. Some of the devices built with crystals of TGS family are (i) Intruder alarms (ii) Fire alarms (iii) Pollution monitoring and gas analysis (iv) Radio meters (v) Laser detectors (vi) Pyroelectric thermal imaging (vii) Pyroelectric vidicon and (viii) Pyroelectric arrays.

3. Synthesis and growth of TGS and phosphate mixed TGS crystals

An investigation has been made to modify the physical properties of Triglycine sulphate (TGS) by substituting phosphate ions for sulphate ions in various concentrations. On considering the ionic radii of sulphur (0.26A°) and phosphorus (0.31A°), Fang etal (1983) have grown L-alanine doped TGS crystals with partial substitution of PO_4^{-3} ions (ATGSP) which have shown significant improvement in the quality of the crystals. Investigation on new derivatives of TGS have been reported in which most of them are aimed at developing materials with high pyroelectric coefficient (p) and low dielectric constant ($\in$) in order to improve the pyroelectric figure of merit ($p/\in$). However, the literature on phosphate substituted TGS crystals without any organic additive is scarce. The present investigation is aimed at growing TGSP crystals without any organic additive and examining the ferroelectric behavior of TGS crystals with and without phosphate in order to find out whether phosphate addition has improved the performance of the IR detector.

Triglycine sulphate (TGS) was synthesized by taking the annular grade glycine (CH_2NH_2COOH) and concentrated sulphuric acid (H_2SO_4) though it has been frequently observed in the literature that TGS is grown from solution with excess sulphuric acid, our trials have been carried out with TGS synthesized in stoichiometric ratio. Glycine and sulphuric acid were taken in the ratio 3:1 respectively. The required volume of concentrated sulphuric acid was diluted with triple distilled water as prepared. Then the calculated amount of glycine salt was slowly dissolved in the diluted sulphuric acid. This solution was heated until the salt crystallized. Extreme care was taken while crystallizing the salt to avoid oxidation of glycine; solution temperature was always maintained below 600 °C. Again the crystallized salt was dissolved in distilled water and then recrystallized. By this way, the impurity content of TGS was minimized. The reaction between glycine and sulphuric acid is given as below:

$$3(NH_2CH_2COOH) + H_2SO_4 \dashrightarrow (NH_2CH_2COOH)_3.H_2SO_4$$

$$3(NH_2CH_2COOH) + (1-x)\,H_2SO_4 + xH_3PO_4 \dashrightarrow (NH_2CH_2COOH)_3.\,(H_2SO_4)_{1-x}.\,(H_3PO_4)_x$$

Triglycine sulpho-phosphate (TGSP) $(NH_2CH_2COOH)_3$ $(H_2SO_4)_{1-X}$ $(H_3PO_4)_{1-X}$ compound was synthesized by reacting the appropriate quantities of glycine, sulphuric acid and phosphoric acid with different compositions. The chemical reaction is given as follows:

$TGS_{1-x}\,P_x$ salts were synthesized with x varying from 0 to 1 in steps of 0.25. Pure TGP salt did not crystallize. It was in the highly viscous glassy state. The synthesized salt was used to grow the crystals.

The temperature of the solution was controlled to an accuracy of ±0.01°C by an optically heated constant temperature bath) the growth rate of TGS is anisotropic; it is high along the polar 'b' axis; comparing the growth of 'a' and 'c' axes, the latter has less growth rate. The substantially lower growth rate of the {001} faces shows that the growth of these faces is energetically more difficult and the crystallization is probably, in this case, limited by the process of stacking the growth units on the crystal surface.

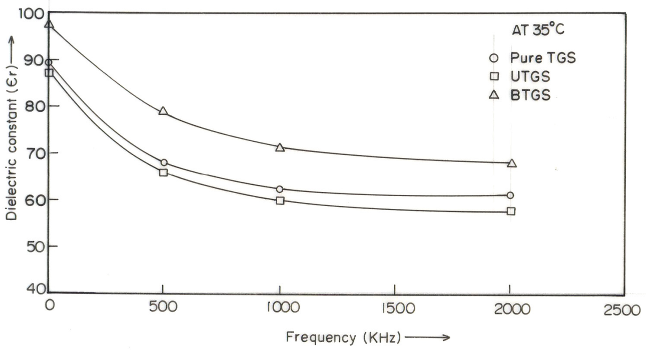

Fig. 1. Dielectric studies.

In the case of TGSP crystals, the solution yielded only small crystals with obvious inclusions at higher concentrations of phosphoric acid (x>0.5). Pure triglycine phosphate solution yielded only aggregates of poly-crystals. Hence the phosphate substitution was restricted in the solution to TGS Estimation of sulphur and phosphorus in the grown crystals by induction coupled plasma revealed that the phosphate ions were not readily absorbed into the crystal; the incorporation of phosphate in the crystal was found to be only 3.5% whereas 85.5% of sulphur entered into the lattice; it may be due to the larger ionic radius of phosphorus (0.31^{0}A) than that of sulphur (0.26^{0}A).

The addition of phosphoric acid improved the growth of TGSP compared to pure TGS in two major aspects; one is the delay in the formation of microbes (organic impurities) and the other is the enhanced growth rate of the crystal. Growth of microbes in TGS has been suppressed by the addition of hydrogen peroxide (H_2SO_4) to the mother liquor periodically, as in the case of L- arginine phosphate (LAP) and potassium dihydrogen phosphate (KDP) crystals (Sasaki et al 1990). But the addition of hydrogen peroxide was not needed for the growth of phosphate-substituted TGS crystals as the shelf life of the solution was found to be extended (Ravi et al 1993). The phosphate substituted crystal exhibited enhanced growth rates along all the axes compared to that of TGS crystal. Hence, the cleavable ac plane in TGSP crystal was larger in area. Fang et al (1983) have also reported enhanced growth rate for alanine mixed TGSP (ATGSP) crystals. The phosphate substituted crystals have also been found to be free from inclusions which are frequently observed in pure TGS crystals. When the molar concentration of phosphoric acid in the solution was higher than that of sulphuric acid, the growth rates of the crystals steeply fell, resulting in tiny crystals. On the basis of the measured dependence of the linear growth rate upon the super saturation, it was proposed that the growth of (110) face was probably controlled by volume diffusion of the molecules towards the surface of the growing crystal and the surface diffusion was responsible for the low growth rates of {001} faces.

3.1 Growth of metal doped TGSP crystals

Triglycine sulphate is a dipolar ferroelectric, that is, it derives its ferroelectric, py-roelectric and piezoelectric properties from the fact that the molecular dipoles are oriented in such a way in the crystal that the unit cell has a dipole moment. The variations occur in the unit cells inside which dopant molecules are probably present which, in turn, causes the variation in resultant dipole moment and hence probable variation in most of the ferroelectric properties of TGS crystals. The presence of either Cu^{2+}, Mg^{2+}, Fe^{3+} or Cr^3+ in the solution of TGS affects the crystal habit and physical properties of the grown crystals (Moravec et al 1971). Doping could create a large number of defects in the TGS lattice which inhibit the rearrangement of the domain structure and thereby stabilize the physical properties of the crystal. A significant contribution to the changes in the ferroelectric properties of TGS under the influence of doping is attributed to the change in both the number of dipoles per unit volume and the unit dipole moment. Doping TGS with either Cu^{2+} or Mg^{2+} enhanced the pyroelectric figure of merit (Moravec et al 1971) which indicated an increase in sensitivity of the pyroelectric IR detectors using this material. The influence of metallic dopants on the electrical properties of TGSP crystals has been studied for four metal ions.

3.2 Growth of amino mixed TGS crystals

In Triglycine sulphate, glycine is one of the amino acids. The substitution of another amino acid - alanine - in the place of glycine has been found to improve the crystal properties by way of contributing to effective internal bias in these crystals which, in turn, inhibits ferroelectric switching giving permanently poled single domain crystal. This improved the device characteristics and hence alanines mixed crystals of TGS family have been investigated by many researchers (Fang et al 1983). The spontaneous polarization of ferroelectric crystal originates from the dipole moment of each dipole within the crystal. Some molecules with high dipole moments can be introduced into the polar lattice of TGS crystal in such a way that their polar orientation tends to coincide with that of bulk polarization. Thus, the pyroelectric properties of the crystal may be improved. In the present investigation, the molecules of amino acids such as alanine, valine, histidine and arginine whose molecular structures are introduced in the TGS crystal. These materials which are also amino acids with larger asymmetric molecules stimulated us to study their influence on the dielectric, pyroelectric and piezoelectric studies. One of the aromatic compounds, aniline ($C_6H_6NH_2$) was also introduced in TGS lattice.

Synthesized TGS salt has been used for the preparation of solution. Any one of the amino acids mentioned above or the aromatic compound -aniline -was added to the saturated TGS aqueous solution till the equilibrium was achieved; the equilibrium concentrations of these additives at 40°C were found to be in the range of 4-5g/l00ml for L-alanine, L- valine and L-histidine in saturated TGS solution. The pH of the solution was then adjusted to 2.3. The solution has then been filtered with 0.2 micron porosity nuclear filter after due preheating. This solution was maintained at 60°C for 2 days prior to loading the crystallizer. Slow cooling method was adopted for the growth of crystals. All the growth parameters, i.e., saturation temperature, volume of solution, impurity concentration, weight of the seed, rate of temperature lowering and the rate of stirring were kept identical during the growth of pure and mixed crystals so as to compare t effect of additives on the growth and properties of the resulting crystals. After completion of the growth run, the crystals were removed from solution and slowly cooled to room temperature. Transparent and high optical quality crystals were obtained. Alanine doped crystal was found to grow with different rates along positive and negative 'b' axes; negative 'b' axis grew at a faster rate than the positive axis. Due to fast growth of crystal along the negative 'b' axis, series of inclusions and cracks have been observed. Positive 'b' axis was transparent and clear. Valine, histidine, arginine and aniline mixed TGS were free from such variation in growth rate. Transparent single crystals were ob in 30-40 days. The amino mixed crystals also showed reduced growth rates in all the faces. Alanine substituted crystal has many bunches of inclusions which multiply the imperfection in the lattice and thereby increased the growth rates of the faces of the crystal.

4. Results and discussion

Equimolar concentrations of the two acids were taken along with the required quantity of glycine in the mother liquor. The concentration of the metal dopants which are taken in the form of corresponding sulphate was l000ppm in the saturated TGS solution. Crystals were grown by lowering the temperature of the water bath. The incorporation of dopants into the crystals has been estimated by chemical analyses. The morphology of the doped crystals was same as that of pure TGS crystal but the growth rates in all the directions were found reduced. When a solute crystallizes from its supersaturated solution, the presence of impurities can often have a spectacular effect on the crystal growth kinetics. The impurities exhibit a marked specialty in their action as they are absorbed into growing crystal surfaces. Absorption of impurities into crystal faces changes the relative surface free energies of the face and may block sites essential to the incorporation of new solute molecules into the crystal lattice and hence slow down the growth.

Powder X-ray diffraction studies were carried out for the as grown crystals using a Rich Seifert X-ray diffractometer with CuK$_\alpha$ (λ = 1.5405 Å) radiation. The FT-IR spectra of all the crystals were recorded from solid phase samples on Shimadzu–800, FTIR spectrometer using 1064nm output of a cw diode pumped Nd:YAG laser as a source of excitation in the region 400 – 4000 cm^{-1} operating at 200mW power at the samples with a spectral resolution of 2 cm^{-1}. The frequency for all sharp bands is accurate to ± 1 cm^{-1}. Kurtz SHG test was performed to find the non- linear optical property of TGS (doped with L-alanine). The crystal was illuminated using Spectra – Physics Quanta-Ray DHS2 Nd-YAG laser, using the first harmonics output of 1064 nm with a pulse width of 8 ns.

5. Conclusions

Crystals of triglycine sulphate (TGS), triglycine sulpho- phosphate (TGSP), metal doped TGSP and amino acid mixed TGS crystals have been grown from aqueous solution. The addition of phosphoric acid has delayed the problem of formation of microbes in the mother liquor. Enhanced growth rates along the 'a' and 'c' axes on phophate substitution yielded larger crystals with wider ac plates usable in thermal detection and imaging. Chemical analyses of the crystals proved that phosphate ions were not readily absorbed into the crystal. The poor stability of the solution at higher concentration of H restricted the composition of the solution to TGS for the growth of bulk single crystals. Metals doped TGSP crystals have been grown and they did not affect the morphology of the pure TGSP crystal. The presence of metal ions in the doped crystals has been estimated by chemical analyses and it was found that the concentration of metal ions was more in the crystal due to the formation of complex of glycine chelates. The amino molecules which have similar structure of glycine were introduced in TGS solution. L-alanine mixed TGS crystals showed different growth rates along positive and negative 'b' axes. Other amino acids mixed crystals did not show any such anisotropy. X-ray Laue pattern confirmed the single crystallinity of the grown crystals.

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