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The effect of nitric acid (HNO_3) on growth, spectral, thermal and dielectric properties of triglycine sulphate (TGS) crystal

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ABSTRACT

The effect of nitric acid (HNO_3) addition on the growth of triglycine sulphate (TGS) crystal has been studied from the aqueous solution for various concentrations of nitric acid. Significant changes in the crystal size and morphology have been observed in all the grown samples. Single crystal and powder X-ray diffraction analyses confirm the structure and cell parameter values of pure and HNO_3 doped TGS crystals. FT-Raman and FTIR spectra confirm the characteristics absorption bands of pure and HNO_3 doped TGS crystals. The composition of TGS crystals have been confirmed by CHNS analysis. Physical properties such as thermal, dielectric and mechanical studies have been performed for the pure and HNO_3 doped TGS crystals. The dielectric constants of the crystals have been studied as a function of frequency. The results suggest that the HNO_3 is doped into TGS crystal and that the doping increases its dielectric constant.

1. Introduction

Triglycine sulphate (TGS) crystal with the chemical formula $(CH_2NH_2COOH)_3{\cdot}H_2SO_4$ is very important for application in pyroelectric detection. Due to low cost, low power requirement and a wide operating range of temperature and frequency, TGS material have been used in IR devices [1]. TGS shows second order phase transition at the Curie point $T_c = 49\,^{\circ}C$. In ferroelectric phase below the Curie point the symmetry is monoclinic with space group $P2_1$. Above T_c, the structure gains an additional set of mirror planes in the space group $P2_1/m$ [2]. According to the structural analysis of ferroelectric triglycine sulphate, there are two kinds of glycine group, glycinium ions and zwitter ions. Such configuration of glycine ions interconnected by short O–H···O hydrogen bonds are regarded as particularly important for the ferroelectric behavior of this crystal [3]. A disadvantage of these crystals is the tendency of their polarization to spontaneous reversal. Therefore, studies dealing with the influence of doping TGS crystals on their physical properties are of particular interest. In recent years, the interest in studying pure and doped TGS crystals has increased because of their promise in various devices.

Several dopants such as urea [4], palladium [5], lutetium [6] ammonium dihydrogen phosphate [7] have been recently used, more or less successfully, to inhibit the ferroelectric switching of TGS, in order to increase crystal unipolarity and the figure of merit of TGS. Many of the additives cause habit modification, but do not effect significant changes in properties [8]. This invariance is due to the fact that TGS substantially reject most additives, which must be present in various concentrations in solution before significant quantities will be incorporated in the crystal [9]. Fang et al. [10] have reported ionic substitution, i.e., phosphorus for sulfur in the TGS structure. Phosphoric acid substitution was found to have a marginal influence on the spontaneous polarization of the TGS. Mohan Kumar et al. [11] reported that the phosphate substituted TGS crystal leads to increase in T_c, i.e., 52.5 °C. In the present work, we have chosen nitric acid as dopant because the nitrate ions are reported to play a partial role for the spontaneous polarization in DGN crystal [12] and the nitric acid can be expected to increase dielectric constant and T_c due to its intrinsic dipole moment. The objective of the present work was to investigate the effect of HNO_3 addition on the growth, spectral, thermal, dielectric and mechanical properties of TGS crystals.

2. Experimental

Triglycine sulphate was synthesized by taking the analar grade glycine (99%) and sulphuric acid according to the reaction:

$$3(NH_2CH_2COOH) + H_2SO_4 \rightarrow (NH_2CH_2COOH)_3{\cdot}H_2SO_4.$$

The doped samples were prepared by mixing fixed amount of nitric acid (10, 20, 30, 40 and 50 mol%) with glycine and sulphuric acid according to the chemical formula:

$$3(CH_2NH_2COOH) + (1-x)H_2SO_4 + xHNO_3 \rightarrow (CH_2NH_2COOH)_3{\cdot}1-xH_2SO_4{\cdot}xHNO_3$$

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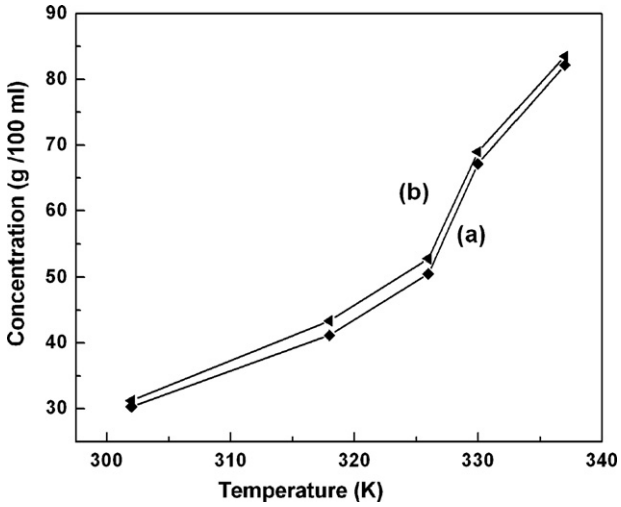

Fig. 1. Solubility curves of (a) pure and (b) 20 mol% HNO_3 added TGS.

x = 0.1, 0.2, 0.3, 0.4 and 0.5 M for 10, 20, 30, 40 and 50 mol%, respectively.

Impurity content in TGS was minimized by successive recrystallization process. As the growth rate of a crystal depends on solubility and growth temperature, the solubility of pure and nitric acid added TGS in double distilled water were determined at various temperatures (Fig. 1). The solubility of HNO_3 added TGS is slightly higher than that of pure TGS. This observation is in accordance with the fact that the solubility can be improved with the use of compatible acids. In both cases, positive slope of the solubility curve enables growth by either slow cooling or slow evaporation; in this work slow evaporation method was chosen [13]. The supersaturated solution was filtered using 0.1 μm porosity filter papers and kept in beakers covered with perforated sheets. The supersaturated solutions in beakers were placed in the constant temperature bath set at 30 °C. The pH value of the saturated TGS solution was found to be 2.02. In case of HNO_3 added TGS solution, the pH values increased with increase in HNO_3 concentrations; 2.03, 2.04, 2.06 and 2.08 for 10, 20, 30, 40 and 50 mol% added HNO_3, respectively. The controlled evaporation of the solvent at constant temperature (30 °C) yielded crystals in the time span of 7–15 days. All the growth experiments were carried out under identical growth condition. The grown crystals were carefully harvested and then subjected to characterization studies.

The grown crystal was subjected to single crystal X-ray diffraction using Nonius CAD-4/MACH 3 diffractometer, with Mo Kα radiation. Powder XRD pattern was recorded on Bruker diffractometer within the 2θ range of 10–80° using Cu Kα as X-ray source (λ = 1.5406 Å) to confirm crystal quality and to identify the cell parameters. TGS crystals grown with and without HNO_3 were powdered and mixed with KBr pellets for obtaining transmission spectra in the mid-IR region (4000–400 cm^{-1}) using Perkin-Elmer (Spectrum RX1) and FT-Raman spectra was recorded using NEXUS670. The C, H, N and S content of grown crystals were determined by using Vario EL III CHNS analyzer. Thermogravimetry of samples was performed using TA instruments SDT Q600 V8.3. The dielectric studies on pure and HNO_3 doped TGS single crystal was carried out using the instrument Phase Sensitive Multiplier built by Newton Fourth Limited (N4L). Micro-hardness measurements were carried out on the grown crystals using Shimadzu tester.

3. Results and discussion

3.1. Crystal growth

Fig. 2 shows the growth habit of without and with HNO_3 added TGS crystals. Shape and size of the grown crystals changed significantly with the change in the amount of HNO_3 in TGS solution. It can be noticed that the morphology of the 10 mol% HNO_3 added TGS crystal (Fig. 2b) is slightly distorted when compared to pure crystal (Fig. 2a). Further increase in HNO_3 concentration (20–40 mol%) leads to crystals with irregular shapes and bunch of crystals grew like cluster. Additives can affect the crystal growth rate by adsorbing onto the surfaces of a growing crystal or by altering solution properties, crystal–solution interfacial tension and aggregation of solute molecules in solution. In addition, anisotropic effects of addi-

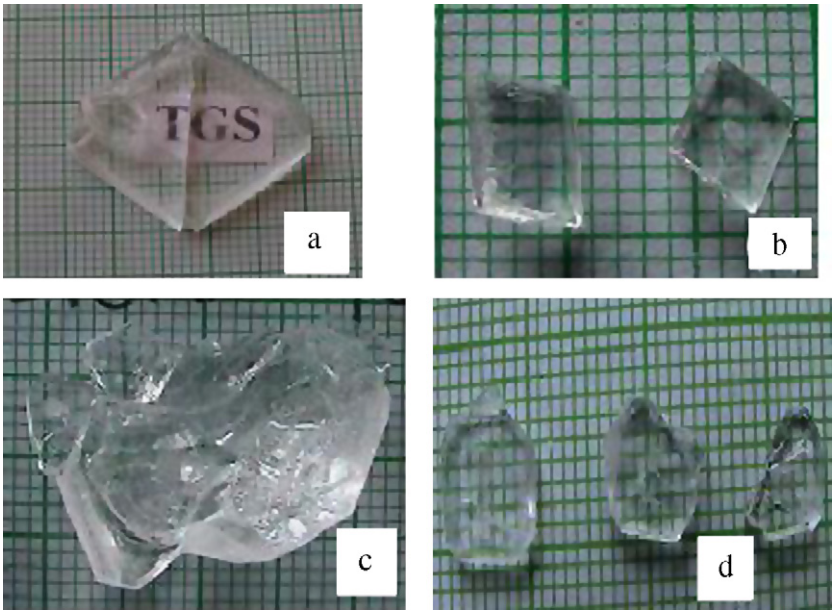

Fig. 2. TGS crystals grown with different concentration of HNO_3; (a) 0 mol%, (b) 10 mol%, (c) 20 mol%, and (d) 50 mol%. The morphology of the 10 mol% HNO_3 added TGS crystal (b) is slightly distorted when compared to pure crystal (a). Further increase in HNO_3 concentration (20–40 mol%) leads to crystals with irregular shapes and bunch of crystals grew like cluster.