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Studies on triglycine sulfate (TGS) crystals doped with sodium bromide (NaBr) grown by solution method

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Abstract: Triglycine sulfate (TGS) crystals, with or without sodium bromide (NaBr) doping, were grown from aqueous solutions by slow evaporation method. The structural characterization was carried out by single crystal XRD method and found that all the grown crystals crystallize in monoclinic structure. The pure and NaBr-doped TGS crystals were also subjected to microhardness, dielectric studies, measurement of density and atomic absorption spectroscopic studies.

Keywords: TGS, crystal growth, NaBr, XRD studies,

Introduction

Triglycine sulfate (TGS) crystal is an interesting ferroelectric and pyroelectric material, which exhibits strong absorbing ability in the most part of infrared region. Due to this property, it is used for the fabrication of infrared detectors and pyroelectric vidicon tubes operating at room temperature. It also finds applications in the fabrication of capacitors, transducers and sensors. TGS crystal shows a typical second-order ferroelectric phase transition at the Curie point T_c=49 ^oC. Below the T_c, TGS possesses the polar point symmetry of group 2 of the monoclinic system, spontaneous polarization P_s arises along the b-axis and above T_c, it possesses the non-polar point group 2/m of the monoclinic system (Selvarajan *et al*., 1993; Alexandru *et al*., 2002; Balamurugan *et al*., 2007). TGS crystal has some disadvantages over doped TGS crystals such as i) the ferroelectric domains possess high mobility at room temperature therefore it is necessary to stabilize domains, ii) easy depolarization by electrical, mechanical and thermal means and iii) microbial contamination with time during the growth. In order to overcome these disadvantages, variety of dopants such as amino acids, organic and inorganic compounds have been introduced in TGS crystals to achieve effective internal bias to stabilize the domains and to get desired pyroelectric and ferroelectric properties (Fang *et al*., 1993; Abu-El-Fadl, 1999; Ashok K Batra *et al*., 2003; Berbacaru *et al*., 2005; Raghavan *et al*., 2008). Since so far alkali halides such as KCl, KBr, NaBr have not been introduced into TGS crystal by other researchers to modify its various physical and chemical properties, in this work, growth and characterization of NaBr-doped TGS crystals have been carried out and the effect of the dopant on the growth, structural, mechanical, dielectric properties have been investigated.

Materials and methods

Synthesis, solubility measurement and growth

An aqueous solution of TGS was prepared using analar reagent (AR) grade of glycine and concentrated sulphuric acid in the molar ratio of 3: 1. The solvent used in this work was de-ionized water. Synthesized TGS salt was obtained by heating the solution of TGS at 50 ^oC. Temperature as low as 50 ^oC was maintained in order to avoid decomposition of the salt. The chemical reaction for obtaining TGS salt is given below:

$$3\,(NH_2CH_2COOH) + H_2SO_4 \rightarrow NH_2CH_2COOH)_3\,(H_2SO_4)$$

To obtain sodium bromide-doped TGS salt, 0.2 mole % , 0.6 mole % and 1 mole % of sodium bromide(NaBr) was added separately to the solution of TGS.

The purity of the synthesized salt of undoped and NaBr-doped TGS was improved by successive re-crystallization. The re-crystallized salt of TGS was dissolved in 50 ml of de-ionized water in an air tight container for the measurement of solubility. Solubility study was carried out using a hot plate magnetic stirrer and a digital thermometer. Here the temperature was controlled using a voltage regulator attached to the magnetic stirrer (accuracy is $\pm$ 0.1 ^oC). Initially, the solution was kept at 30 ^oC and stirred continuously using the magnetic stirrer for about 3 hours. After attaining the saturation, the solubility was determined gravimetrically (Selvarajan *et al*., 2008). The same procedure was followed for other temperatures and for NaBr-added TGS samples.

Growth of undoped and NaBr-doped TGS crystals was carried out by solution method with slow evaporation technique at room temperature (30 ^oC). The twice re-crystallied salts of undoped and NaBr-doped TGS were used to prepare the saturated solutions separately in accordance with the solubility data. The solutions were constantly stirred for about 3 hours using a magnetic stirrer and were filtered using 4 micro Whatmann filter papers. Then the filtered solutions were kept in borosil beakers covered with porous papers and the beakers were kept in an undisturbed place. The allowed growth period was about 25 to 30 days.

Characterization methods

Unit cell parameters of undoped and NaBr-doped TGS crystals were obtained by employing a Nonius CAD-4 / MACH 3 single crystal X-ray diffractometer, with MoKα radiation (λ=0.71073 Å) at room temperature. The dimensions of the single crystal used for this analysis were of the order of 0.5 mm × 0.5 mm × 0.3 mm^3. Transparent and good quality crystals were selected for dielectric studies. Density was measured by the floatation method (Ramachandran & Natarajan, 2004). Atomic Absorption Spectroscopic (AAS) measurements were carried out using Perkin-Elmer spectrophotometer to determine the metal ion contents of the grown NaBr-doped TGS crystals.

The capacitance (C_{crys}) and dielectric loss factor (tan δ) measurements were carried out using the parallel plate capacitor method (John *et al*., 2008) at various

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temperatures ranging from 30 to 70 °C using an Agilant 4284A LCR meter at a constant frequency of 1000 Hz. The sample cleaved perpendicular to the polar axis (b-axis) was used. Opposite faces of the sample crystals were coated with good quality graphite to obtain a good conductive surface layer. The samples were annealed before making observations in the holder assembly at 55 °C for about 30 minutes to remove moisture content if present. The dimensions of the crystals were measured using a traveling microscope (LC =0.001 cm). Air capacitance (C_{air}) was also measured. The dielectric constant (ε_r) of the crystal was calculated using the relation (as the crystal area was smaller than the plate area of the cell)

$$\varepsilon_r = \left\{ \frac{C_{crys} - C_{air}\,(1 - A_{crys}/A_{air})}{C_{air}} \right\} \frac{(A_{air})}{(A_{crys})} \quad \text{---- (1)}$$

where C_{crys} is the capacitance with crystal (including air), C_{air} is the capacitance of air, A_{crys} is the area of the crystal touching the electrode and A_{air} is the area of the electrode.

The mechanical hardness studies of the grown crystals were estimated using Leitz Weitzler hardness tester fitted with a diamond indenter. Smooth, flat surface was selected and subjected to this study on the (010) plane of both pure and NaBr- doped TGS crystals. Indentations were made for various loads from 5 g to 25 g. Several trials of indentation were carried out on the prominent face and the average diagonal lengths were measured for an indentation time of 10 seconds. The Vickers micro hardness number was calculated using the relation $H_v = 1.8544\ P/d^2$ kg/mm^2, where P is the applied load and d is the diagonal length of the indentation impression (Dhanaraj *et al.*, 2008).

Results and discussion

The samples synthesized and solubility in de-ionized water was measured by gravimetrical method. It is observed that solubility increases with temperature for all the samples and it is found to be more in NaBr-doped TGS crystals than that for the pure TGS crystal (Fig.1). Hence it is clear that in the case of doped samples, the solvent is able to accommodate a marginally increased amount of solute for the saturation at the same temperature.

In accordance with the solubility data, saturated solutions were prepared and crystal growth was carried out at room temperature by slow evaporation technique. The grown crystals are found to be transparent and colourless. Their shape and size are sensitive to the amount of NaBr in the solution during the growth. All the grown crystals have been observed to be polyhedron in shape (Fig.2). Morphological alterations have been observed in the NaBr-doped TGS crystals compared to pure TGS crystals.

Fig.1.Solubility diagram for the samples

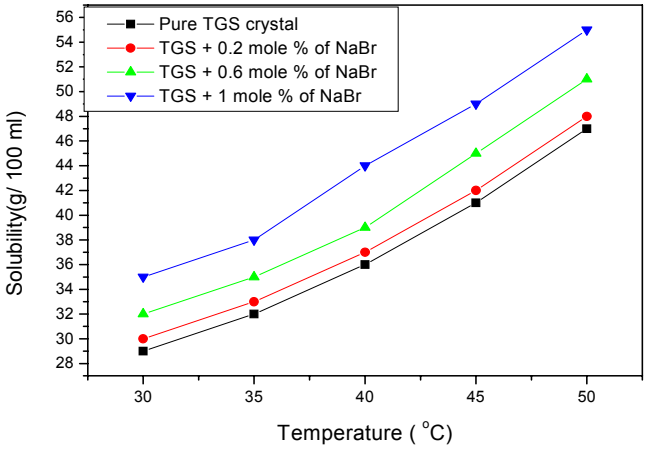


Fig.2. Grown crystals of this work

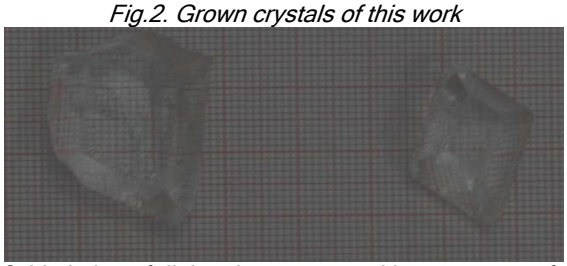


Fig.3. Variation of dielectric constant with temperature for the grown crystals at the constant frequency of 10^3 Hz

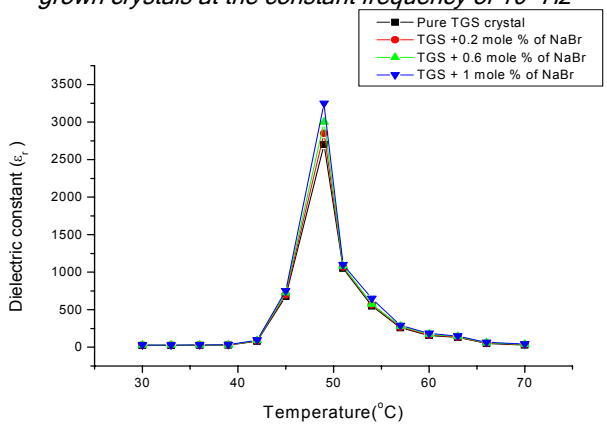
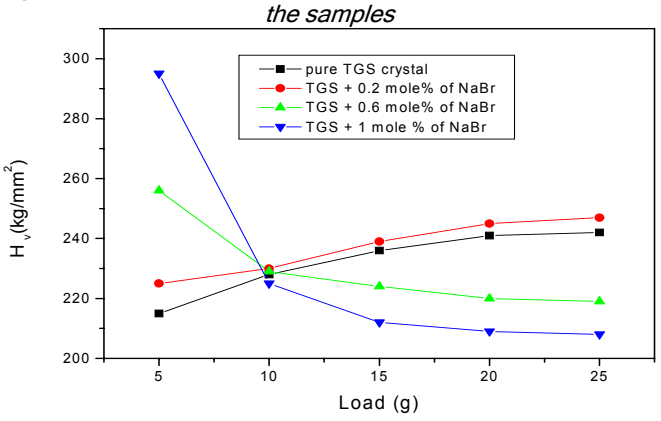


Fig. 4. Variation of hardness number with the applied loads for the samples



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The grown crystals were subjected to single crystal XRD analysis and single crystalline data were obtained from least-squares refinement of the setting angles of 25 reflections. From the data, it is observed that pure and NaBr-doped TGS crystallizes in monoclinic system and the calculated unit cell parameters are listed in Table 1. The obtained values of lattice parameters for the pure TGS crystal are found to be in good agreement with the earlier report (Sun *et al*., 1999). No systematic variation was observed in the values of lattice parameters when TGS crystals are doped with NaBr.

Table 1. Lattice parameter values of undoped and NaBr-doped TGS crystals

Sample	a (Å)	b (Å)	c (Å)	β (^{0})
Undoped TGS	9.392	12.734	5.784	109.45
TGS+ NaBr (0.2 mole %)	9.353	12.614	5.821	108.44
TGS + NaBr (0.6 mole%)	9.384	12.658	5.899	110.49
TGS+NaBr (1 mole %)	9.445	12. 711	5.812	111.55

Density of the grown crystals have been measured by floatation method and the obtained values are presented in the Table 2. The values of density are found to increase as the concentration of dopant (NaBr) increases. It may be due to the incorporation of dopants in the interstitial positions of the sample. When the dopant occupies the crystal lattice, the mass is expected to increase and so the density. For the impurity-added systems considered in the present study, the density increases when the doping concentration increases. The density variation clearly shows that the impurity ions have entered proportionately into the TGS crystals as per the impurity concentration considered for the aqueous solution used for the growth of single crystals.

The metal (Na) content in the grown doped crystals is estimated by Atomic Absorption Spectroscopic (AAS) (Table 2). This study confirms the presence of Na in the doped TGS crystals.

Table 2. Values of densities and metal atom contents

Sample	Density (g/cc)	Metal (Na) content (ppm)
Undoped TGS crystal	1.675	- -
TGS + 0.2 mole % of NaBr	1. 684	182
TGS + 0.6 mole % of NaBr	1.703	354
TGS + 1 mole % of NaBr	1.708	745

Fig. 3 shows the temperature dependence of dielectric constant for pure and NaBr-doped TGS crystals. The Curie temperature, T_c for all the samples was observed to be 49 ^{o}C. The dielectric constant is small at low temperature, which increases with temperature and rises sharply up to the Curie point. The rapid increase may be due to the space charge polarization of thermally generated carriers. Above T_c, the dielectric constant decreases suddenly. It is observed that there is no change in the Curie temperature and increase of dielectric constant at the Curie point when TGS crystals are doped with various concentration of NaBr. The increase in dielectric constant for NaBr-doped TGS crystals may be due to frittering of domains due to incorporation of impurities in the lattice (Muralidharan *et al*., 2002).

Fig. 4 shows the variation of load versus Vickers microhardness number for pure and NaBr- doped TGS crystals. It is observed that in pure TGS crystal, the hardness increases slightly with increase in the load.up to 50 g. For 0.2 mole % of NaBr added TGS crystal, hardness is more than that of pure TGS crystal at all loads up to 25 g. But for 0.6 and 1 mole % of NaBr added TGS crystals, the hardness is high at lower loads and then it decreases with increasing of load. This may be the result of loosely packed lattice with reduced bond energy due to the introduction of NaBr into the lattice of TGS. For loads above 25 g, cracks started developing around the indentation mark..

Conclusions

Pure and NaBr-added TGS salts were synthesized and solubility studies were carried out for the prepared samples in de-ionized water in the temperature range from 30 to 50 ^{o}C. In accordance with the solubility data, saturated solutions were prepared for growing pure and NaBr-doped TGS crystals by slow evaporation technique. XRD studies reveal the monoclinic structure of the grown crystals. Density of grown crystals was measured by floatation method and results show that there is an increase of density values when TGS crystals are added with NaBr. Atomic absorption study confirms the presence of sodium in the lattice of doped TGS crystals. It is observed from dielectric studies that there is no change of Curie point when TGS crystals are doped with NaBr. Mechanical property of the grown crystals has been studied by microhardness test and noticed that there is an increase of microhardness number for 0.2 mole % of NaBr added TGS crystal where as hardness decreases for 0.6 and 1 mole % of NaBr added TGS crystals.

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References

1. Abu El-Fadl A (1999) Effect of divalent-ions-doping on the absorption spectra parameters of triglycine sulphate crystals. *J. Phys. Chem. Solids* 60, 1881-1893.
2. Alexandru HV and Berbecaru C (2002) Fundamentals in ferroelectric transition of TGS. *Materials Sci. Semicon. Proces*. 5, 159-165.
3. Ashok K. Batra, Mohan D. Aggarwal and Ravindra B. Lal (2003) Growth and characterization of doped

DTGS crystals for infrared sensing devices. *Materials Letters.* 57, 3943-3948.

4. Balamurugan N, Lenin M, Bhagavannarayana G and Ramasamy P (2007) Growth of TGS crystals using uniaxially solution-crystallization method of Sankaranarayanan-Ramasamy. *Crystal Res. Technol*. 42, 151-156.
5. Berbacaru C, Alexandru HV, Pintilie L, Dutu A, Logofatu B and Radulescu RC (2005) Doped versus pure TGS crystals. *Materials Sci. Engg*. B11, 141-146.
6. Dhanaraj PV, Santheep K. Mathew and Rajesh NP (2008) Nucleation studies and characterization of potassium dihydrogen phosphate with L-arginine monohydrochloride as additive. *J.Cryst. Growth*. 310, 2532-2536.
7. Fang CS, Liu H, Zhuo HS, Wang M and Xu D (1993) A New modified TGS crystal. *Cryst. Res. Technol*. 30, 785-789.
8. John NJ , Selvarajan P, Benita Jeba Silviya S and Mahadevan CK (2007) Growth and characterization of disodium hydrogen orthophosphate (DSHP) single crystals. *Mat. Manufact.Process*. 22, 379-383.
9. Muralidharan R, Mohankumar R, Ushasree P M, Jayavel R and Ramasamy P (2002) Effect of rare-earth dopants on the growth and properties of triglycine sulphate crystals. *J.Crystal Growth*. 234, 545-550.
10. Raghavan CM, Sankar R, Mohan Kumar R and Jayavel R (2008) Effect of amino acid doping on the growth and ferroelectric properties of triglycine sulphate single crystals. *Materials Res. Bulletin*. 43, 305-311.
11. Ramachandran E, Natarajan S (2004) Crystal Growth of some urinary stone constitiuents; *In-vitro* crystallization of L-cystine and its characterization. *Cryst. Res. Technol.* 39, 308-312.
12. Selvarajan P, Siva Dhas A, Freeda TH and Mahadevan CK (2008) Growth, XRD and dielectric properties of triglycine sulpho-phosphate (TGSP) crystals added with magnesium sulfate. *Physica B*. 403, 4205-4208.
13. Selvarajan P, Das BN, Gon HB and Rao KV (1992) Dielectric properties of quenched and X- ray irradiated triglycine sulphate single crystals later excited with last light. *J.Mat. Sci. Lett*. 11, 1312-1314.
14. Sun X, Wang M, Pan QW, Shi W, Fang CS (1999) Study on the growth and properties of quanidine doped triglycine sulfate crystal. *Cryst. Res. Technol*. 34, 1251-1254.