

# Growth, structural, optical and microhardness study of KCl doped triglycine sulphate (TGS) crystals for photonic applications

H. N. DAS, J. PODDER<sup>a\*</sup>

*Materials Science Division, Atomic Energy Centre, Dhaka-1000*

*<sup>a</sup>Department of Physics, Bangladesh University of Engineering and Technology, Dhaka-1000, Bangladesh*

Single crystals of pure triglycine sulphate (TGS) and KCl doped TGS were grown from aqueous solutions by slow evaporation technique. The concentrations of KCl in the TGS mother solution were varied from 0.2 to 1.0 mol%. The grown crystals were examined by energy dispersive X-ray (EDX) to find out the presence of doping elements in the crystals. The presence of functional groups in the grown crystals was identified by Fourier Transform Infrared Spectroscopy. The lattice parameters were determined by powder X-ray diffraction and reveals that the crystals are belong to monoclinic structure. The UV-visible transmittance spectra were carried out on the grown crystals. A sharp fall in the optical transmittance is observed at 240 nm for pure TGS and all KCl doped TGS crystals and there is no shift of the lower cut off wavelength value. The optical band gap of TGS is found to be 5.0 eV. The mechanical strength of the grown crystal has been analyzed by Vickers microhardness measurement.

(Received June 14, 2012; accepted September 18, 2013)

*Keywords:* TGS Crystal; KCl, Solution growth, EDX, XRD, UV-vis studies

## 1. Introduction

Triglycine sulfate (TGS) and its isomorphs crystals have been considered as promising materials due to its excellent ferroelectric and pyroelectric properties [1]. TGS single crystals are most suitable materials for making detectors of IR radiation, earth observation cameras, astronomical telescopes, etc. [2]. TGS crystal also finds application in the fabrication of capacitors, transducers, sensors, storage devices and laser devices [3-4]. For laser energy meters and VIDICON applications, large area plates perpendicular to the polar axis, typically discs shape between 2.5 and 7.5 cm in diameter are required [5]. It is observed that undoped TGS crystals have disadvantages over doped TGS crystals such as high mobility of ferroelectric domains at room temperature, easy depolarization by electrical, mechanical and thermal means, and microbial contamination with time during the growth and low Curie point, etc. [6-7]. 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 [8-10]. Many metallic ion dopants such as  $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Mn}^{2+}$ , and  $\text{Ni}^{2+}$  have been added to modify the properties of TGS crystals [11-12]. Rare earth metal ions such as La, Ce and Nd modified the morphology and coercive field values [13]. The growth phenomenon of a large size and good quality TGS crystals along (001) and (010) facet have been reported using unidirectional SR method [14-15]. Potassium chloride (KCl) as dopant is found to improve

the optical quality and morphology of the crystals [16-18]. To the best of authors' knowledge, there is no report on the growth of TGS doped with KCl. In this paper, KCl has been introduced into TGS crystal to see the effect of KCl on the morphological, structural, optical and mechanical properties of TGS crystals.

## 2. Experimental details

### 2.1 Materials synthesis

Analytical reagent (AR) grade glycine and concentrated sulfuric acid in the molar ratio of 3:1 were used to synthesize TGS crystal. Hence the solution was prepared at 50°C and the temperature was maintained at this value to avoid the decomposition of the salt. The solution was transferred to a big tray and allowed to evaporate. Within 5 days 80% of the solvent was evaporated and the synthesized TGS material was collected. The recrystallized TGS material was dissolved again in triple distilled water to crystallize pure TGS crystal.

### 2.2 Growth of crystal

Single crystals of pure TGS and KCl doped TGS were grown by slow evaporation technique at room temperature. The recrystallized salt of TGS was dissolved in deionized water to prepare the mother solution and constantly stirred for about 2 hours using a magnetic stirrer and then filtered using 4 micron Whatman filter paper. The filtered solution was kept in a Borosil beaker covered with porous paper to

get slow evaporation. After 2~3 days, transparent and good quality seed crystals were produced. To grow KCl doped TGS crystals, 0.2, 0.4, 0.6, 1.0 mol % KCl separately added into the saturated solution of TGS and the solution was allowed to evaporate to grow crystals for a period of 25 to 30 days. The harvested crystals are displayed in Fig. 1. It is noticed that grown crystals are found to be transparent and colorless. All the grown crystals have been observed to be polyhedron in shape. Slight morphological changes viz. flat plate shapes have been observed in the KCl doped TGS crystals as compared to that of pure TGS crystals.

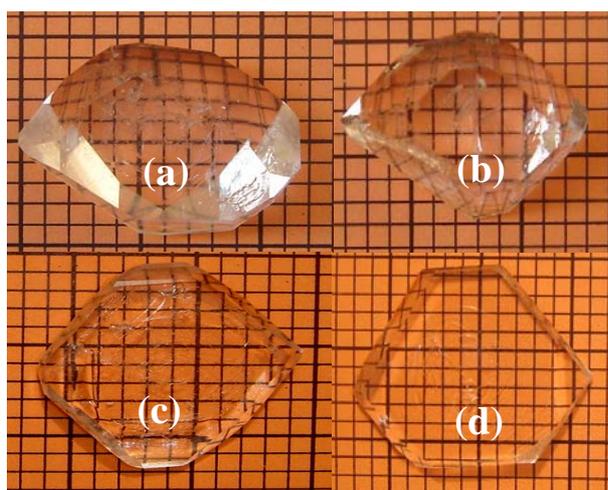


Fig. 1. Photograph of (a) pure TGS, (b) 0.2 mol % KCl, (c) 0.4 mol % KCl, and (d) 1 mol % KCl doped TGS crystals.

### 2.3 Characterization

The FTIR spectra were recorded using a Shimadzu FT-IR 8400 spectrophotometer in the wave number region  $4000 - 400 \text{ cm}^{-1}$  at room temperature using the KBr pellet technique. A Philips X'pert PRO X-ray diffractometer system with  $\text{CuK}_\alpha$  ( $\lambda=1.54178 \text{ \AA}$ ) radiation with an operating voltage of 40 KV and the tube current of 30 mA was used. Scanning rate was maintained at  $2^\circ\text{-}20/\text{min}$  and the scan angle was  $10\text{-}40^\circ$ . The identification of elements in the pure and doped crystals was detected by an energy dispersive spectrometer Quanta Inspect S-12919 system. The optical properties of the grown crystals were studied using a SHIMADZU UV-160A in the wavelength range 190 to 1100 nm with a polished crystal of  $5 \times 5 \times 2 \text{ mm}^3$ .

## 3. Results and discussion

### 3.1 EDX spectra

Single crystals of pure and 0.6 mol % KCl doped TGS were used for obtaining the spectra of EDX, shown in Fig. 2 (a) and (b). The EDX spectra of TGS crystal show the corresponding elements of TGS crystals, which indicate the pure-phase of the TGS sample. The spectrum of doped crystal shows the presence of K and Cl as doping

element and suggesting that K and Cl are entered into the lattice of TGS crystals.

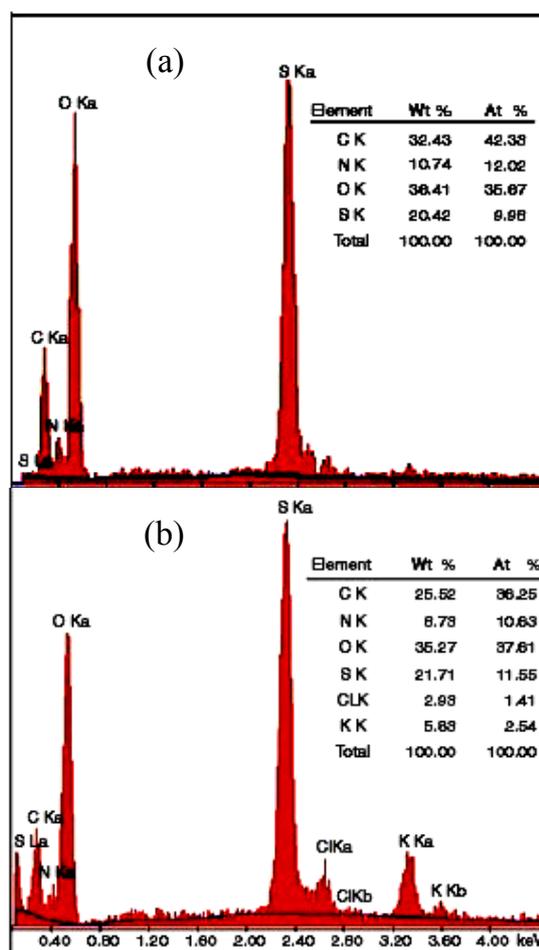


Fig. 2. EDX spectra of (a) pure TGS crystals (b) KCl doped TGS crystals

### 3.2 FTIR analysis

The FTIR spectra of pure TGS and KCl doped TGS are shown in Fig. 3. The broad and strong absorption band is observed in the region  $2100 - 3800 \text{ cm}^{-1}$  due to overlapping of N-H asymmetric stretching vibration of  $\text{NH}_3^+$  ion at  $3161 \text{ cm}^{-1}$  and also O-H stretching vibration. The absorption band at  $1710.3 \text{ cm}^{-1}$  is due to C = O stretching vibration. The broad absorption band in the region 1610 to  $1450 \text{ cm}^{-1}$  can be assigned to COO-vibrational mode and  $\text{CO}_2$  [O-C=O] asymmetric stretching. The bending modes of  $\text{CH}_2$  are positioned at  $1377.1$  and C-O-H bending vibration at  $1426.6 \text{ cm}^{-1}$ . The intense and sharp absorption bands appeared between  $1120\text{-}1130 \text{ cm}^{-1}$  are assigned to stretching mode of sulfate ions. The peaks observed at  $615.2$ ,  $572.8$ , and  $499 \text{ cm}^{-1}$  is due to  $\text{NH}_3^+$  oscillation. The band at around  $650 \text{ cm}^{-1}$  represents the presence of  $\text{Cl}^-$  ion. In the spectrum, the presence of chlorine is very clearly identified and the peak area corresponds to  $\text{Cl}^-$  ion is

increasing with the increase of KCl molar concentration. It seems that Cl<sup>-</sup> ion is adsorbed into the lattice sites.

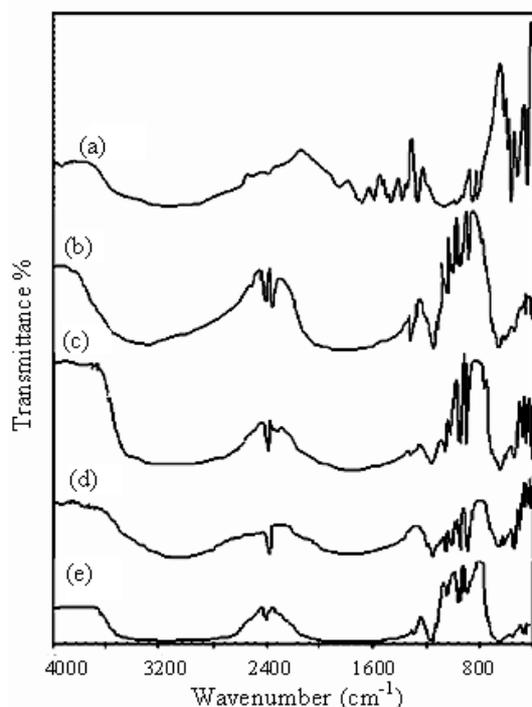


Fig. 3. FTIR spectra of (a) pure TGS, (b) 0.2 mol % KCl, (c) 0.4 mol % KCl, (d) 0.6 mol % KCl, and (e) 1 mol % KCl doped TGS crystals.

### 3.3 Powder XRD analysis

Powder X-ray diffraction analysis has been carried out to confirm the crystallinity and also to identify the lattice parameters. Intensity versus  $2\theta$  recorded for pure TGS and KCl (0.2, 0.4, 0.6 and 1 mol %) doped TGS single crystals are shown in Fig. 4. The lattice parameters are determined

for all the samples and are given in Table 1. The lattice parameters for the pure TGS crystal are found to be in good agreement with the reported value [19]. The crystalline structure of pure TGS and KCl doped TGS are found to be in monoclinic system and the unit cell volumes are more or less same. It indicates that impurity ions might have entered into the TGS crystal matrix and slightly distorted the regular structure of the TGS crystal.

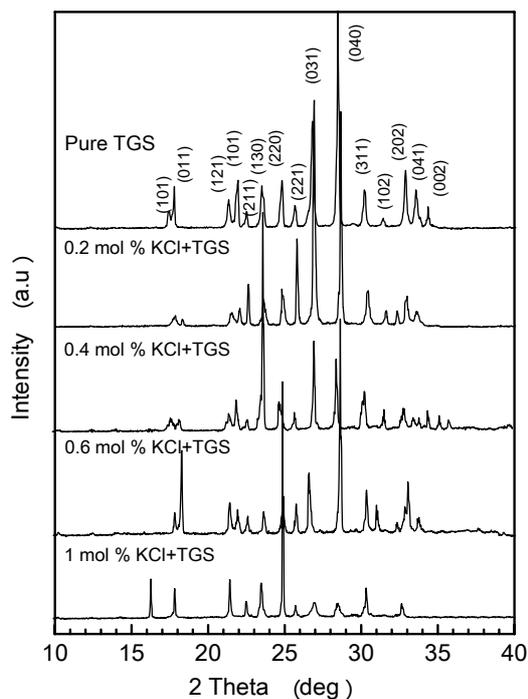


Fig. 4. Powder X-ray diffraction pattern of pure and KCl doped TGS

Table 1. The lattice parameters of pure and doped TGS crystals

Sample	a(Å)	b(Å)	c(Å)	$\beta(^{\circ})$	Volume of unit cell, $V(\text{Å}^3)$
Pure TGS	9.4454	12.5608	5.7043	109.517	637.8912
0.2 mol % KCl + TGS	9.3888	12.4847	5.6975	108.413	633.6641
0.4 mol % KCl + TGS	9.3427	12.5180	5.6999	113.688	610.4484
0.6 mol % KCl + TGS	9.4380	12.4744	5.6770	110.250	627.0641
1 mol % KCl + TGS	9.3474	12.5332	5.6955	107.609	635.9790

### 3.4 Optical studies

The recorded transmittance spectra of pure and KCl doped TGS crystals in the wavelength range 190 -1100 nm are shown in Fig. 5. For all the crystals, a cut off wavelength was found at 240 nm. The band gap is calculated using the formula,  $E_g = 1240/\lambda$  eV and found to be about 5.0 eV [19]. It is observed that the magnitude of energy gap for undoped and doped TGS crystal are same

and the band gap values are found in good agreement with the reported literature [19]. KCl doped TGS crystal (0.6 mole % KCl and above) reduces the transmittance in the visible range and hence absorbance is increased in the entire UV-Visible region of the spectra in compared to spectrum of pure TGS crystals. This may be attributed to the internal vibration groups of TGS: K<sup>+</sup> ions or the phonon frequency of the phonons which may interact most strongly in the absorption process considerably changes

with doping. The improvement in the transmission of the doped crystal may be due to lesser defects compared to pure TGS crystal. Lesser dislocation density (DD) which in turn reduced scattering centres in the KCl doped TGS crystals and increases the output intensity [20-21].

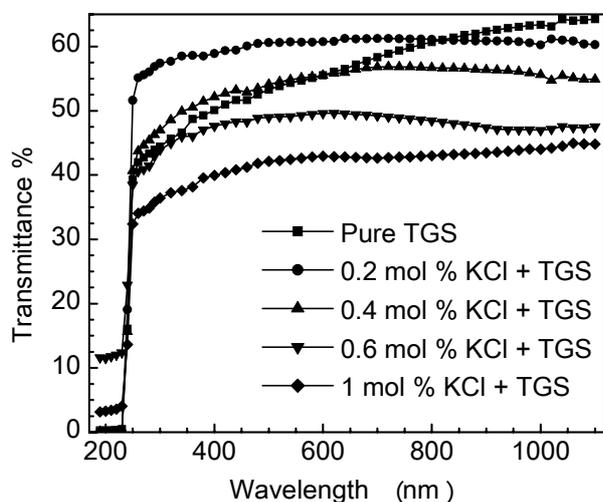


Fig. 5. UV transmittance spectra of pure and KCl doped TGS crystals

### 3.5 Microhardness studies

Vickers microhardness values are calculated from the following relation

$$H_v = 1.854 \frac{P}{d^2} \text{ kg/mm}^2$$

where  $H_v$  is the Vickers microhardness value,  $P$  is the applied load in Kg,  $d$  is the mean diagonal length of the indentation mark in mm and 1.8544 is a constant of a geometrical fraction for the diamond pyramid. The indentations were made on the 001 face of the TGS crystals at room temperature with the load ranging from 25 g to 100 g. A graph between hardness value ( $H_v$ ) and applied load ( $P$ ) is drawn in figure 6. It is observed that at lower loads, hardness is found to be increased, which may be attributed to the work hardening of the surface layers. For pure TGS crystals, the hardness increases with load up to 50g. For loads above 50g, cracks started developing and the indentation mark. It may be due to the release of internal stress generated locally by indentation. The similar results are observed by the other researchers [22]. For 0.2 mol % of KCl doped TGS crystal, hardness is found more than that of pure TGS crystal at all loads up to 50g. But for 0.6 and 1.0 mole % KCl doped TGS crystals, the hardness are high at lower loads and then it decreases with the increase of load. This may be the result of loosely packed lattice with reduced bond energy due to the introduction of KCl into the matrix of TGS crystals. An increase in the mechanical strength for doped TGS crystals will have significant effect on fabrication of IR devices

and processing such as ease in crystal polishing and less wastage due to cracking/ breakage while polishing [23].

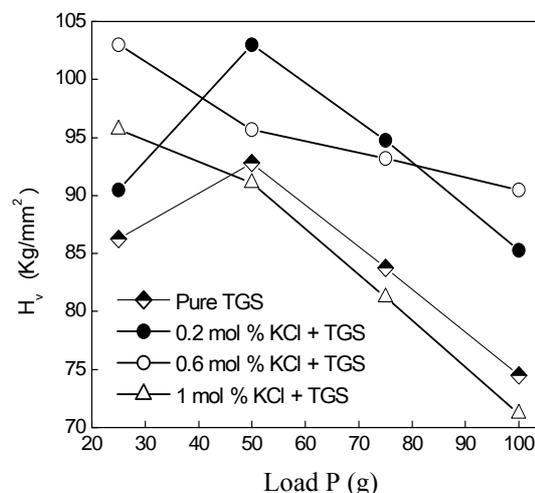


Fig.6. Variation of hardness number with the applied load for KCl doped TGS crystals.

### 4. Conclusions

Optical quality single crystals of pure TGS and KCl doped TGS crystals were grown from aqueous solutions by slow evaporation method. All the grown crystals are found chemically stable, defect free, optically transparent and colorless. The stoichiometric compositions of the grown crystals were examined by EDX. FTIR spectra confirm the presence of functional groups of the grown crystals. X-ray diffraction analysis reveals that the structure of the grown crystal is monoclinic. The optical transmission spectra recorded on the grown sample, the sharp absorption onset at 240 nm and the optical transmission in the wavelength range 200 to 1100 nm exhibit the optical quality and suitability of the crystal for use in detector instruments. The optical transmittance is found to be reduced in the visible range with KCl doping concentration and mechanical hardness is also increased for low concentration. The results explored from the laboratory grown TGS crystal are expected to be useful in the photonics industry.

### Reference

- [1] N. Balamurugan, M. Lenin, G. Bhagavannarayana, P. Ramasamy, *Cryst. Res. Technol.* **42**, 151 (2007).
- [2] V. V. Efimov, V. V. Ivanov, E. A. Klevtsova, N. N. Novikova, V. V. Sikolenko, *Part Nucl, Lett.* **6**, 65 (2002).
- [3] N. Nakatani, *Jpn. J. Appl. Phys.* **32**, 4268 (1993).
- [4] R. W. Whatmore, *Rep. Prog. Phys.* **49**, 1335 (1986).
- [5] S. Satapathy, S. K. Sharma, A. K. Karnal, V. K. Wadhawan, *J. Cryst. Growth* **240**, 196 (2002).
- [6] M. A. Gaffar, A. A. Al-Fadl, S. A. Mansour, *J. Phys.*

- D: Appl. Phys. **34**, 915 (1999).
- [7] L. Prokopova, J. Novotny, Z. Micka, V. Malina, Cryst. Res. Technol. **36**, 1189 (2001).
- [8] S. Aravazhi, R. Jayavel, C. Subramanian, Ferroelectrics, **200**, 390 (1997).
- [9] Genbo Su, Youping He, Hongshi Yao, Zikong Shi, Qingin Eu, J. Cryst. Growth, **209**, 220 (2000).
- [10] K. Biedzycki, Solid State Commun., **118**, 141 (2001).
- [11] K. L. Bye, P. W. Whipps, E. T. Keve, Ferroelectrics, **4**, 253 (1972).
- [12] J. Eisner, Ferroelectrics, **17**, 575 (1978).
- [13] R. Muralidharan, R. Mohankumar, P. M. Ushasree, R. Jayavel, P. Ramasamy, J. Cryst. Growth, **234**, 545 (2002).
- [14] M. Senthil Pandian, N. Balamurugan, V. Ganesh, P.V. Raja Shekar, K. Kishan Rao, P. Ramasamy Mater. Lett., **62**, 3830 (2008).
- [15] M. Senthil Pandian, P. Ramasamy, Binay Kumar, Mater. Res. Bull., **47**, 1587 (2012).
- [16] J. Podder, J. Cryst. Growth **237**, 70 (2002).
- [17] J.Podder, S. Ramalingom, S. Narayana Kalkura, Cryst. Res. Technol. **36**, 549 (2001).
- [18] S. Ferdous and J. Podder, J. Bangladesh Academy of Sciences **33**, No. 1, 47 (2009).
- [19] K. Balasubramanian, P. Selvarajan, Rec. Res. Sci. Tech. **2**, 06 (2010).
- [20] M. Senthil Pandian, P. Ramasamy, Mater. Chem. Phys., **132**, 1019 (2012).
- [21] M. Senthil Pandian, P. Ramasamy, J. Cryst. Growth, **312**, 413 (2010).
- [22] N. Theresita Shanthi, P. Selvarajan, C. K. Mahadevan, Indian J. Sci. Technol., **2**, No. 3, 0974 (2009).
- [23] M. Senthil Pandian, K. Boopathi, P. Ramasamy, G. Bhagavannarayana, Mater. Res. Bull. **47**, 826 (2012).

---

\*Corresponding author: jpodder@phy.buet.ac.bd