

Effect of swift heavy ion irradiation on dye doped thiourea -TGS crystals for IR detector and laser applications

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Triglycine sulphate (TGS) crystals were grown by slow evaporation process. The stability of TGS single crystal was improved by doping organic dyes. The structural, optical properties, pyroelectric properties and dielectric properties of the doped crystals were analyzed. The FTIR spectra of all grown crystals have been recorded in the range of 400 - 4000 cm⁻¹ using Bruker FT-IR 8400 spectrophotometer by KBr pellet technique. To determine the lattice parameters, powder X-ray diffraction analysis was performed by X-ray diffractometer system with Cu-K_α (λ = 1.54178Å) radiation at room temperature with an operating voltage 40 kV and the tube current was 30 mA. In the present work, optical transmission and absorption spectra were recorded by Systronics UV-Double beam spectrometer in the wavelength range 190 to 1100 nm. The results for doped TGS crystal are compared with the results of the pure TGS crystals. The doped crystals show good second harmonic generation efficiency. The dopants increase the hardness value of the material, which also depends on the concentration of the dopants. Dye doping improves the Nonlinear Optical properties of the grown crystals. Results of the growth kinetics of Thiourea crystals in the presence of impurities are also discussed.

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1. Introduction

The study of Ferro electricity has been closely linked with device applications [1]. The pyroelectric properties of ferroelectrics make them very suitable for thermal detection. This can be used to detect any radiation that results in a temperature change of the crystal [2]. They also have useful features at room temperature operation TGS has been the most extensively studied material for thermal detector applications. The presence of hysteresis loop makes them possible to use ferroelectrics as memory elements in computers [3]. The ferroelectric materials can be used as a thermo static non-linear dielectric element. They can be used to measure pressure and can also be used as frequency multiplier [4].

The potential barrier which a system must overcome in order to create a (crystalline) nucleus in the ideally homogeneous mother phase and which determines the rate of nucleation is defined as homogenous nucleation, by the interface energy. TGS crystals are at present the only ferroelectric crystals [5], which can be grown easily in bulk form needed for IR imaging applications; for which (010) planes of size (2×1) cm² are required (fig.1). There are problems associated with the growth of bulk transparent TGS crystals by traditional technique, due

primarily to formation of spurious nucleation and irregular growth rate.

The purpose of the present investigation on nucleation is mainly to determine the induction period of pure and methyl orange doped TGS solutions under those conditions, which are present during the growth of large TGS crystals [6]. A quantitative experimental investigation of nucleation is extremely complicated. This is due primarily to the small sizes of the nuclei; which as yet make it impossible to observe them directly and measure the condensation parameters [7]. Triglycine sulphate (NH₂CH₂COOH)₃.H₂SO₄ crystals are very important because of their application as room temperature IR detectors and imaging systems[8]. The ferroelectric property of TGS was first discovered by Matthias et al 1956. This crystal 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 [9].

In TGS, the spontaneous electrical polarization is along the [010] crystallographic direction, which is sensitive to the temperature variation. In recent years, there has been considerable development in infrared detectors, with the aim of achieving the highest performance. To further enhance the device parameters, TGS has been doped with amino acids. For the fabrication

of thermal detectors and imaging systems, large size TGS crystals of wide b-plane are required, for which studies on fundamental growth parameters such as the solubility, detestable zone width are very essential[10]. There are many reports on ferroelectric studies on TGS such as the pyroelectric, dielectric properties etc., but investigations on the basic growth parameters such as the solubility and metastable zone width of pure and doped TGS are very scarce [11].

In the present study, an investigation was made on the solubility and metastable zone width for pure and methyl orange doped TGS saturated solutions [12]. The results of the investigations form a basis for the growth of bulk TGS crystals [13]. The effect of seed of different orientations on the habit of c and the change of morphology while doping with amino acids has also been investigated [14].

2. Crystal structure and properties of TGS

TGS $[(\text{NH}_2\text{CH}_2\text{COOH})_3\cdot\text{H}_2\text{SO}_4]$ is a colourless, odourless and acidic salt[15]; it is synthesized by Glycine acid with sulphuric acid in the molar ratio of 3:1[16]. Its density is 1.65 - 1.68 g/cm^3 TGS belongs to the monoclinic system with the space group P_{21} number of formula units per unit cell is 2. Above the Curie temperature ($T = 47^\circ\text{C}$), the monoclinic system and belongs to the centro-symmetric crystal class $P_{21/m}$. So the spontaneous polarization is then lost [17]. Below T_c , the mirror plane disappears and the crystal belongs to the polar point group P_{21} of monoclinic system.

The first detailed investigation of crystal structure was carried out. TGS may be called glycine-di-glycinium sulphate with chemical formula

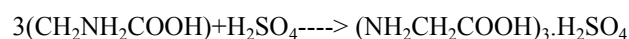


Of the three-glycine group contained in the asymmetric unit, two assume a completely planar configuration and the third on assume partially planar configuration [18]. They are connected by a hydrogen bond between oxygen atoms. The bonds between two planar groups II and III are responsible for ferroelectric transition [19]. 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 mirror image [20].

2.1 Synthesis of TGS salt

TGS was synthesized by taking the analar grade glycine ($\text{CH}_2\text{NH}_2\text{COOH}$) and concentrated sulphuric acid (H_2SO_4) Glycine and sulphuric acid were taken in the ratio 3:1 respectively. The required volume of concentrated sulphuric acid was diluted with millipore water. Then the calculated amount of glycine salt was slowly dissolved in the diluted sulphuric acid. This solution was heated until the crystallized. Extreme care was taken while

crystallizing the salt to avoid oxidation of glycine; solution temperature was always maintained below 60°C [21]. Again the crystallized salt was dissolved in Millipore water and then recrystallized. By this way, the impurity content of TG was minimized. The reaction between glycine and sulphuric acid is given below



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.

2.2 Experiment

Recrystallized salt was used to study the solubility of pure and xlylenol orange doped TGS for three different temperatures 35, 40 and 45°C . A sealed container charged with millipore water and the solute, maintained at a constant temperature, was used to determine the equilibrium concentration. The solution was stirred continuously for 24 hours. The content of the solution was analyzed gravimetrically. The grown crystal was shown in Fig. 1.



Fig. 1. Xlylenol dye doped TGS crystal

In Triglycine sulphate-Thiourea, glycine is one of the amino acids. The substitution of another dye – xlylenol orange - in the place of glycine has been found to improve the crystal properties by the way of contributing to effective internal bias in these crystals which, in turn, inhibits ferroelectric switching giving permanently poled single domain crystal[22]. This improved the device characteristics and hence Xlylenol orange mixed crystals. The spontaneous polarization of ferroelectric crystal originates from the dipole moment of each dipole within the crystal [23]. Some molecules with higher dipole moments can be introduced into the polar lattice of TGS crystal in such a way that their polar orientation tends to

coincide with the bulk polarization [24]. Thus, the pyroelectric properties of the crystal may be improved.

3. Results and discussion

3.1 X-ray analysis

The grown crystals have been characterized by powder X ray diffractometer. Fig. 2 represents the powder X-ray pattern of the grown TGS. The system is found to exhibit monoclinic structure with the space group P_{21} and the lattice parameters of pure TGS crystal are $a = 9.581 \text{ \AA}$, $b = 11.450 \text{ \AA}$ and $c = 4.936 \text{ \AA}$ which are in good agreement with the literature. TGS pure and doped crystals were cleaved into small pieces [25]. The radiation used was $\text{MoK}\alpha$, monochromatized by graphite. Cell parameters were measured from 30 reflections and after refining the orientation matrix and cell parameters by least squares [26]. The following data have been obtained for TGS-Thiourea crystal both pure and Xylenol doped from the XRD analysis [27].

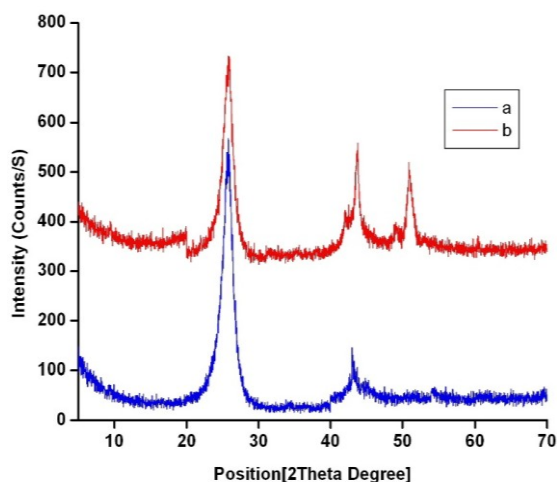


Fig. 2. XRD of (a) Pure and (b) Xylenol orange doped TGS-Thiourea Crystal.

3.2 UV-visible studies

The UV-VIS spectrum analysis has been measured using Systronics UV-Vis double beam spectrophotometer in the wavelength range of 200 – 1200 nm. The UV-VIS spectrum gives limited information about the structure of the molecule because the absorption of UV and visible light involves promotion of the electron in σ and π orbital from the ground state to higher energy states [28]. To find the transmission range of Xylenol orange doped TGS-Thiourea wavelengths between 200 and 1200 nm was recorded. The recorded optical transmission spectrum was shown in Fig. 3. The transmittance is found to be maximum in the entire visible and infrared regions. When we consider the percentage of transmission we observe that for all Xylenol orange doped TGS-Thiourea crystals the transmission has been increased 75% in the visible region. From the spectrum it is observed that the transmittance percentage of Xylenol orange doped TGS-

Thiourea is 15% higher than that of the pure grown crystal. The crystal shows a good transmittance in the entire visible region. The lower cut-off at 280 nm combined with the above, attest the usefulness of this material for optoelectronics applications and the second harmonic generation of the Nd :YAG laser and for the generation of the higher harmonics of the laser diodes [29]. A good optical transmittance is very desirable in a nonlinear optical (NLO) crystal since the absorptions, if any, in an NLO material near the fundamental or the second harmonic of an Nd: YAG laser, 1064 nm and 532 nm respectively, will lead to loss of conversion efficiency of second harmonic generation (SHG).

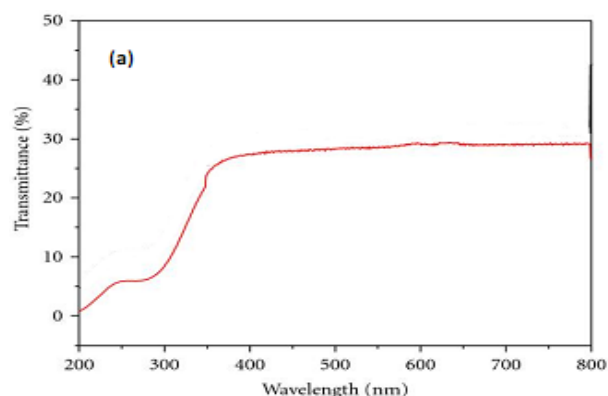


Fig. 3. UV-Visible studies of Xylenol orange doped TGS-Thiourea crystal.

3.3 FTIR studies

The presence of dopants in the crystal was qualitatively investigated by the FTIR studies. The infrared spectra were obtained with a BRUKER IFS 66V FTIR spectrometer using the KBr pellet technique. The FTIR data for pure and dye doped TGS. The NH, OH and CH absorptions smeared into a continuum which occurs at a higher frequency (3100 cm^{-1}). The absorption around 1500 cm^{-1} refers to the normal band position for unionized C=O and hence TGS is not in the Zwitter ion form. The strong absorption in the 1015 - 1175 cm^{-1} region is evidently due to the sulphate part of the molecule.

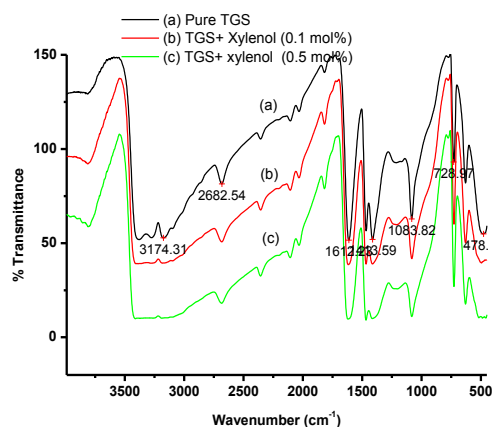


Fig. 4. FT-IR Spectra of pure and Xylenol Orange doped TGS-Thiourea Crystals.

The doping with xylenol orange causes much broadening of the peaks in the spectra compared to the pure TGS crystal. The spectra also reveal reduction in the crystal hardness as a result of dopant incorporation - this has been evident from the hardness measurements for pure and doped crystals. It is inferred that the modes due to

polar groupings, for example COOH, COO are more broadened compared to the modes of non-polar groupings illustrating that the doped crystals reject more degree of interaction for the polar groupings rather than for non-polar groupings.

Table 1. Observed and Calculated IR frequencies (cm^{-1}) of pure TGS and TGS doped with 0.1 mol % of Xylenol orange and 0.5 mol % of Xylenol orange

Species	Calculated frequencies (cm^{-1})	Observed IR frequencies and intensities			
		Pure TGS	TGS doped Xylenol orange (0.1 mol %)	TGS doped Xylenol orange (0.5 mol %)	Assignments
A/E	3791	3790 (w)	3785 (broad)	3789 (Broad)	NH ₂ Asymmetric Stretching in phase
	3425	3430 (vw)	3439 (vw)	3435 (vw)	NH ₂ Asymmetric Stretching out of phase
	3375	3371 (vw)	3369 (VW)	3366 (vw)	NH ₂ Symmetric Stretching in phase
	3295	3290 (vw)	3286 (vw)	3285 (vw)	NH ₂ Symmetric Stretching out of phase
	3225	3222 (vw)	3220 (vw)	3220 (vw)	C-H Stretching
	3175	3174 (w)	3170 (vw)	3165 (vw)	N-H Asymmetric Stretching in phase
	3090	3085 (vw)	3083 (vw)	3081 (vw)	N-H Asymmetric Stretching out of phase
	2875	2873 (vw)	2870 (vw)	2868 (vw)	N-H Symmetric Stretching in phase
	2684	2683 (m)	2680 (m)	2678 (m)	N-H Symmetric Stretching out of phase
	2358	2355 (w)	2352 (w)	2350 (w)	Overtone/combination
	2315	2313 (w)	2315 (w)	2315 (w)	Overtone/combination

3.4 Thermal studies

Fig. 5 illustrates the Differential Thermal Analysis (DTA) and Thermo-Gravimetric Analysis (TGA) curves for the grown TGS-thiourea doped Xylenol crystal. The

DTA curve implies that the material undergoes an irreversible endothermic transition at 200°C where the melting begins. This peak was endothermic peak, represents the temperature at which the melting terminates which corresponds to its melting point at 210°C.

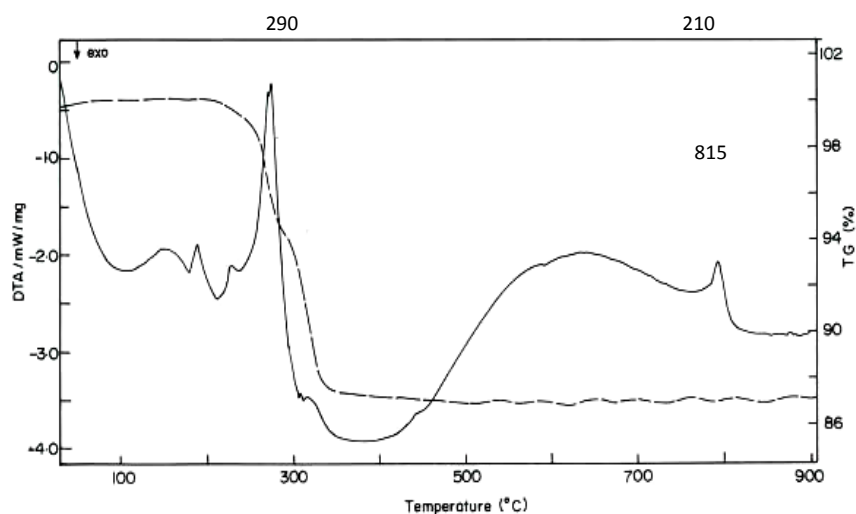


Fig. 5. TGA-DTA curves of TGS-Thiourea doped Xylenol Crystal

Ideally, the melting point of the trace corresponds to a vertical line. The sharpness of the endothermic peak shows good degree of crystallinity of the grown ingot. The exothermic peak at 290°C indicates a phase change from liquid to vapour state as evident from the loss of weight of about 87% in TG curve.

3.5 Poling of the crystals

The poling apparatus consists of a constant temperature silicone oil bath and a high voltage power supply. The sample holder to be used in the silicon oil bath is designed and fabricated using Teflon and suitable electrodes. It is immersed in the silicone oil bath and leads are introduced to the sample of high voltage power supply. The temperature of the bath is controlled by a temperature controller. The temperature of the bath could be set at temperature in the range 30 °C- 400 °C to an accuracy of ± 1 °C. Heat sink copper tube was incorporated in the silicone oil bath for quick cooling to reduce the cooling time between two successive poling processes.

The domain wall contribution to the free energy will affect most of the macroscopic properties of ferroelectrics. Consequently the starting point for the experimental study of a ferroelectric is the preparation of single crystals, which are both single domains electrically and untwined crystallographically. Electric poling was achieved by cooling the crystal from the paraelectric phase into the ferroelectric phase in an applied field parallel to the crystallographic axis under constant electric field (E) conditions, the voltage applied to the electrode sample being 3.5 KV/cm. The single domain state was then thermodynamically stable in an unstressed crystal since depolarization fields were neutralized by charge flow in the external circuit. The amplitude and duration of the voltage required for poling vary substantially between materials.

Some materials will pole easily and if used in large signal switching applications may not even require a preliminary poling cycle. A hysteresis loop illustrating the coercive field E_c , the spontaneous polarization P_s and the remanent polarization P_r .

The power supply was capable of delivering varying voltages from 2 to 50 kV insteps of 0.1 kV. A Teflon disc of a few millimeters thickness along with the silicone sealant was used in the poling cell (sample holder) in order to increase the arcing length and thus avoid arcing. Xylenol orange doped TGS-Thiourea possess a high dielectric constant along the polar axis, which was a function of temperature and reaches to a peak value at the critical temperature (123 K). The ferroelectric transition at the Curie temperature was associated with either the latent heat or anomalous behaviour of specific heat and at critical temperature (T_c) the surface charges appear abruptly. It possess pseudo symmetric structure of polar symmetry and have polar structure in ferroelectric state while non polar structure in para electric state and the ferroelectric crystal possess domain structure which is visible in polarized

light. The domain structures in KDP crystal due to the presence of Xylenol orange doped TGS-Thiourea were analyzed. It was observed that the dopant improves the ferroelectric property in TGS-Thiourea crystal.

3.6 Analysis of pyroelectric studies

The doping of TGS with Xylenol orange has shifted the ferroelectric transition temperature (T_c) to a higher value. The shift observed at Curie temperature may be due to simultaneous change in macroscopic polarization and increase in the electrical conductivity. The dipolar strength of Xylenol orange is larger compared to pure TGS as a result of large electron repulsion from $(CH_3)_2CH$ group. So, Xylenol orange doped TGS is found to have maximum pyroelectric coefficient compared to pure TGS. The doping of dye in the place of glycine makes the crystal set-up an inherent bias field by which the depolarization phenomenon of the crystal can be prevented. In the case of xylenol orange, due to the extra methyl group in the molecule which prevents its rotation within the lattice, the dipolar molecule is fixed with respect to the crystal structure and the polarization does not disappear at a temperature close to T_c which keeps the crystal permanently polarized. The internal bias is produced by two factors; one is the change in the dipolar moment at the site of the dopants and other is the displaced charge in the cells around the doped cells. The second factor has greater influence. The xylenol orange doped TGS exhibited a maximum pyroelectric coefficient at 52°C.

3.7. Dielectric studies

The temperature dependent dielectric constant of xylenol orange doped TGS crystals were measured using Hioki LCR Hi-Tester in the frequency range from 300Hz to 50MHz at different temperatures. In order to ensure good electrical contact between the crystal and the electrodes, the sample was coated with silver paint and mounted between the two electrodes. The capacitance of the parallel plate capacitor formed by the electrodes, with the sample as a dielectric medium, was measured. The variation of capacitance was recorded in the frequency range 300Hz to 50 MHz at different temperatures. The dielectric constant of the material was calculated for different frequencies from the measured capacitance values. It is observed that dielectric constant has high values in the low frequency region and there after decreases with the applied frequency. The very high value of dielectric constant at low frequencies may be due to the presence of all the four polarizations namely, space charge, orientation, electronic and ionic polarization, and the low value at higher frequencies may be due to the loss of significance of these polarizations gradually.

The most commonly measured small signal electrical property is the dielectric permittivity ϵ_r also often referred as the dielectric constant. ϵ_r in polar materials is rarely a constant, but varies with the applied field, stress and temperature and other parameters. When a dielectric

material is subjected to an electric field, the net polarization of the medium is altered. The dielectric constant and dielectric loss may be obtained from a measurement of the real and complex admittance of a crystal. These measurements are particularly straightforward with impedance bridges, which separate the conductance and capacitance of the crystals. Unpoled crystals have been used for the measurement and this is mainly used for the identification of phase transitions and the recording of transition temperature. Any strain or inhomogeneities in the crystal tend to broaden the phase transition so that there is no apparent discontinuity in dielectric permittivity (ϵ_r).

Swift Heavy Ion irradiation can result in change of optical properties of the crystals by several processes, viz., changes in stoichiometry of new phases, structural changes, defects produced by the electronic and nuclear energy loss, volume expansion in the nuclear damage region, stress effects etc.

4. Swift heavy heavy ion irradiation on xylene dye doped TGS-thiourea crystals

In the recent years, 50 MeV Li^{3+} ion irradiation (up to dose of 10^{11} ions/cm²) was used to produce optical wave guides in a large number of materials like oxides (Al_2O_3 , SiO_2), phosphate (KTiOPO_4), niobates (LiNbO_3 , KNbO_3) etc., for use in the optoelectronic technology. In addition, irradiation of higher doses of Li^{3+} ion damages the lattice effectively and the crystalline quality of the irradiated region.

This investigation was carried out to study the effect of swift heavy ion irradiation on the structural, electrical, optical and surface morphology properties of Xylene dye doped TGS-Thiourea crystal. To fabricate optical devices using these materials, a detailed and study of ion induced changes is necessary.

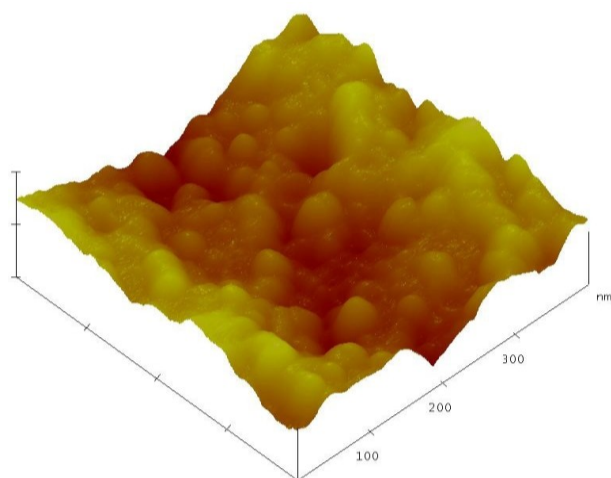


Fig. 6. AFM image of Li^{3+} ions irradiated Xylene dye doped TGS-Thiourea with fluence of 10^{11} ions/cm²

5. NLO studies of Li^{3+} ion irradiated of pure and Xylene dye doped TGS-Thiourea Crystals

SHG measurements were made, using the Kurtz and Perry powder method. The 1064 nm fundamental output from a Q-switched Nd-YAG laser (Quanta Ray) was divided by a beam splitter, where one portion of the light was directed onto a reference cell KDP. The resultant second – harmonic signal (532 nm) was passed through a sharp-cut filter (Corning 527) designed to eliminate any stray visible light from the laser flash pump, and several neutral density filters designed to attenuate the second-harmonic signal, before being focused onto a photomultiplier tube (RCA IP28). The second portion of the fundamental beam was directed on to a second cell containing the sample to be measured. SHG efficiency is improved after the irradiation effect on dye doped TGS crystal. Most irradiation studies in the hydrogen bonded ferroelectrics have been concentrated on the transient defects induced by ionising radiation such as UV light, where the defects are closely related to the optical properties. On the other hand, heavy ion beam irradiation effects have rarely been studied.

Li^{3+} irradiations lead to the development of a well-defined surface H peak in Xylene dye doped TGS-Thiourea. The depletion of hydrogen from the –OH groups of TGS-Thiourea sample in terms of the possible bond-breaking mechanism. Due to beam interaction, electron moves to the conduction band leaving behind the free hole, which can get self-trapped and configurationally changes occurring in the neighbouring structural units. Irradiation effects diffuse the dyes uniformly in the crystal due to lattice disorder. The NLO efficiency is increased in dye doped TGS-Thiourea crystals after irradiation. The stability of dye doped TGS-Thiourea was improved by doping organic dyes. The nano-islands of dyes in TGS-Thiourea are likely to be dissolved and enhance the non-linear optical properties of these materials.

Some molecules with higher dipole moments can be introduced into the polar lattice of TGS crystal in such a way that their polar orientation tends to coincide with the bulk polarization. Thus, the pyroelectric properties of the crystal may be improved. The NLO property in these molecules is due to the virtual electron excitation occurring in the individual molecular or polymeric units. Organic dyes and polymeric materials possess lower dielectric constants and faster response time. Optical quality crystals of La, Ce and Nd-doped TGS crystals have been grown by low temperature solution growth by slow cooling method. Dielectric studies performed on the grown crystals for different frequencies show that NdTGS and LaTGS possess dielectric constant and high pyroelectric coefficient, which makes them suitable for infrared detector applications. Piezoelectric coefficient has been observed for the as-grown crystals without poling.

Irradiation of solids with swift heavy ion (SHI) beams, lead to strong electronic excitation of the target's electron subsystem and the energy loss was mainly determined by the ions interaction with the target electrons. Some observed effects are wrinkles on the solid

surface, surface roughening or smoothing depending on the angle of incidence and directional mass transport. Near-surface lattice defects occur in the interaction of solids with cluster ions due to interference in the electronic energy loss process. At lower energies (KeV range), elastic collisions are dominant and at higher energies (a few tens of MeV), inelastic collisions dominate the energy loss process.

6. Conclusion

In the present investigation, the molecules of dye such as xylenol orange, whose molecular structures are CH_3 (CH) (NH_2) COOH, have been introduced in the TGS crystal. These materials with larger asymmetric molecules stimulated us to study their influence on the basic growth parameters such as solubility and stability. Synthesized TGS salt has been used for the preparation of solution. The dopants xylenol orange were added to the saturated TGS aqueous solution till the equilibrium was achieved.

The pyroelectric studies it was found that doping the crystals with xylenol orange enhanced the pyroelectric coefficient and the ferroelectric transition temperature (T_c). Dielectric studies on the samples reveal a low permittivity of the doped crystals were suitable for IR detector applications. The FTIR studies reveal a broadening of peaks for the doped samples confirming the presence of dopants in the crystal. The substitution of dye - in the place of glycine has been found to improve the crystal properties by the 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 xylenol orange crystals. The spontaneous polarization of ferroelectric crystal originates from the dipole moment of each dipole within the crystal.

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