International Journal of Advanced Research in Physical Science (IJARPS)
Volume 3, Issue 1, January 2016, PP 21-28
ISSN 2349-7874 (Print) & ISSN 2349-7882 (Online)
www.arcjournals.org

Effect of Swift Heavy Ion Irradiation on Coumarine Doped Glycene Zinc Sulphate (GZS) Semi Organic Crystals for Laser Applications

K. Sahadevan[1], D.Narayansamy[2], P.Kumaresan[3] & P.M.Anbarasan[4]

[1, 4] Department of Physics, Periyar University, Salem-636 011, Tamil Nadu, India
[2] Department of Physics, SKP Engineering College, Tiruvannamamalai, Tamil Nadu, India
[3] Department of Physics, Thiru.A.Govindasamy Government Arts College, Tindivanam- 604 002, Tamil Nadu, India
logeshkumaresan@yahoo.com

Abstract: *Nonlinear optical (NLO) crystals have come upon the materials science scene and are being studied by many research groups around the world. Most irradiation studies in the hydrogen bonded have been concentrated on the transient defects induced by ionizing radiation such as UV light, where the defects are closely related to the optical properties. Glycene Zinc Sulphate (GZS) Semi organic single crystals of were synthesized by a slow evaporation technique. Single crystal and powder XRD analyses confirmed the orthorhombic crystal structure. On the other hand, ion beam irradiation effects have rarely been studied. Li^{3+} irradiations lead to the development of a well-defined surface H peak in dye doped GZS crystals. 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 neighboring structural units. Irradiation effects diffuse the dyes uniformly in the crystal due to lattice disorder. The structural, chemical, optical, mechanical and non-linear optical properties of the doped crystals were analyzed with the characterization studies such as powder XRD, FT-IR, UV-Visible, SEM and SHG measurements respectively. The results for doped GZS crystal are compared with the results of the pure GZS crystals.The TGA, DTA shows that the material has good thermal stability; the UV-Vis spectrum shows the transmitting ability of the crystal in the entire visible region. The dielectric constant and dielectric loss were calculated by varying frequencies at different temperature. The microhardness test reveals that the crystals possess good mechanical strength.*

Keywords: *Solution growth, Irradiation, Thermal Studies, micro hardness, Non-linear optical property*

1. Introduction

The search for nonlinear optical (NLO) materials has been of great interest because of their significant impact on laser technology, optical communication and data storage technology [1]. The synthesis of new and efficient frequency conversion materials has resulted in the development of new semi organic materials [2]. Semi organic system provides many structure and bonding schemes for the molecular engineering of new materials. Semi organic nonlinear optical (NLO) crystals are attracting a great deal of attention due to their high NLO coefficient, high damage threshold and high mechanical strength compared to organic NLO crystals.Non-linear optical (NLO) materials have a significant impact on laser technology, optical communication, optical storage technology and electro optic modulation[3]. The search for new frequency conversion materials over the past decade has led to the discovery of many semi organic materials. These materials posses large nonlinearity, high resistance laser induced damage and low angular sensitivity [4, 5]. The semi organic NLO materials gain importance over organic and inorganic NLO materials because of their large polarizability and wide transmission window. Extensive investigation in this direction resulted in the discovery of a new phase match semi organic NLO crystals [6].

GZS crystal finds widespread use as frequency doublers in laser applications and was studied in great detail. Improvement in the quality of the GZS crystals and the performance of these crystal-based devices can be realized with suitable dopants. To analyze the influence of dye based dopant on the non-linear optical property of GZS crystals; efforts were made to dope GZS with Coumarine dye. The effects of impurity atoms on the quality and performance of the crystals were analyzed [7]. Bulk crystals of GZS and dye doped GZS crystals were grown by solution growth technique.

2. Experimental Procedure

2.1. Crystal Growth

Slow evaporation method was employed for growing the single crystals of GZS. Recrystallised salts of glycine and Zinc sulphate and de-ionized water are used in the present crystal growth experiment. Saturated aqueous solutions were prepared at room temperature following the known solubility data. The solubility of glycine and potassium sulphate in de-ionized water (100ml) at room temperatures was 14.75gm. The solutions are mixed in the volume ratio 1:1 for about 5 hours using a magnetic stirrer with 520rpm to ensure a homogeneous temperature and concentration throughout the volume of the solution.

The recrystallized salt was used for the preparation of saturated solution at room temperature (32^{o}C). The solution was filtered by filtration pump and Whatman filter paper of pore size 11 µm. Then the filtered solution was transferred to a petridish with a perforated lid in order to control the evaporation rate and kept undisturbed in a dust free environment. The solvent evaporates slowly leading to supersaturation which in turn initiates the nucleation and the crystal grows.Pure GZS crystals were grown from aqueous solution by slow evaporation and also by slow cooling method (0.5^{0} C/Day). The same method is followed for coumarine doped GZS crystals (0.1 mole % of Coumarine dye). The solubility of doped GZS in the solvent was measured for each dopants, it was found to be 14.5 gms/100 ml at 35^{o}C for Coumarine dye.

Good quality single crystals with size 6.02mm x 2.63mm x 1.81mm were grown in 20 days. The grown single crystal of GZS is shown in the Figure 1.The seed crystals are prepared at low temperature by spontaneous nucleation. The seed crystals with perfect shape and free from macro defects were used for growth experiments. Large single crystals of GZS and doped GZS were grown using constant temperature bath (CTB) controlled with an accuracy of 0.01^{0}C. The mother solution was saturated with the initial pH value, 4.9 for Coumarine dye. The growth was carried out for more than 24 days by keeping the bath at a temperature of 39^{o}C.

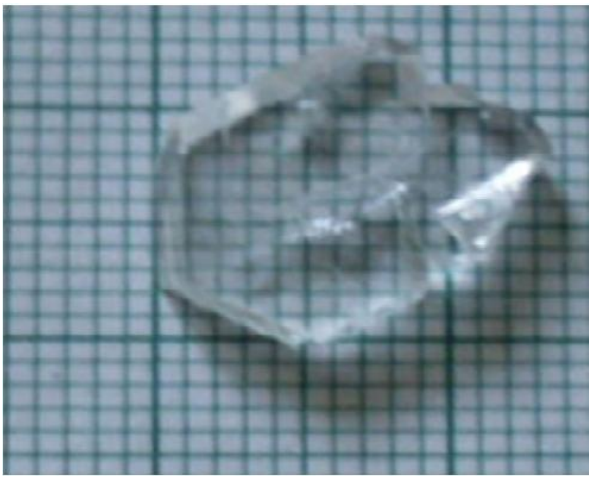

Figure1. *Coumarine doped GZS Crystal*

Single crystal X-ray diffraction analysis for the grown glycine potassium sulphate crystal is carried out to confirm the crystalline nature and also to identify the unit cell parameters using ENRAF Nonius CAD4 single crystal x-ray diffractometer. The calculated lattice parameters are a= 5.77Ǻ b=7.54 Ǻ c=10.04 Ǻ and α=β=γ= 90° and the crystal system was found to be orthorhombic.

2.2. Irradiation Studies

Well-polished, transparent, single crystalline GZS samples, procured from the Advanced Physics Research Laboratory, Thiru.A.Govindasamy Government Arts College, Tindivanam, Tamil Nadu, India, were used for Li^{+} irradiation at room temperature. The samples were irradiated with 20 MeV Li ions by using a Pelletron Accelerator. These studies were performed at room temperature in an experimental chamber under vacuum better than 10^{-7} Torr. The beam was scanned a 10 mm ×10 mm area on the sample using a magnetic beam scanner. The dose of charge accumulated in the sample was measured separately in terms of the fluences and the following fluences were used: 1×10^{11}, 1×10^{12}, 1×10^{13} and 1×10^{14} ions cm^{-2}. According to the calculation of stopping and ranges of ions in matter

(SRIM) [8], the projected range (Rp) of the 20 MeV Li ions in Thiourea is 7.5 µm. Also the corresponding end of range lateral distribution of straggling is 4.567MeV (mg $cm^{-2})^{-1}$ and the longitudinal distribution of straggling is 7.5 MeV $(mgcm^{-2})^{-1}$.

2.3. Characterization Studies

Powder X-ray diffraction studies were carried out for the as grown crystals using Rich Seifert X-ray diffractometer with CuKα (λ= 1.5498 Å) radiation. The FT-IR spectra of all the crystals were recorded from solid phase samples on a Bruker IFS 66V model spectrophotometer using 1064 nm 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 IR spectra were also recorded on Shimadzu–800, FTIR spectrometer series of Japan in the region 400 – 4000 cm^{-1}. The frequencies for all sharp bands are accurate to ± 1 cm^{-1}. The UV-VIS spectrum of GZS, doped GZS crystals were taken in the wavelength 200nm-1200nm ranges using the Varian CARY5E UV-VIS-NIR Spectrophotometer. Nd-YAG laser test was performed to find the non- linear optical property of dye doped GZS crystals. The crystal was illuminated using spectra – physics Quanta-Ray DHS2Nd-YAG laser using the first harmonics out put of 1064 nm with a pulse width of 8 ns.

2.3.1. X-Ray Diffraction Studies

Powder XRD spectra (Fig.2) for the pure and dyes doped GZS revealed that the structures of the doped crystals are slightly distorted compared to the pure GZS crystal. This may be attributed to strains on the lattice by the absorption or substitution of dyes.

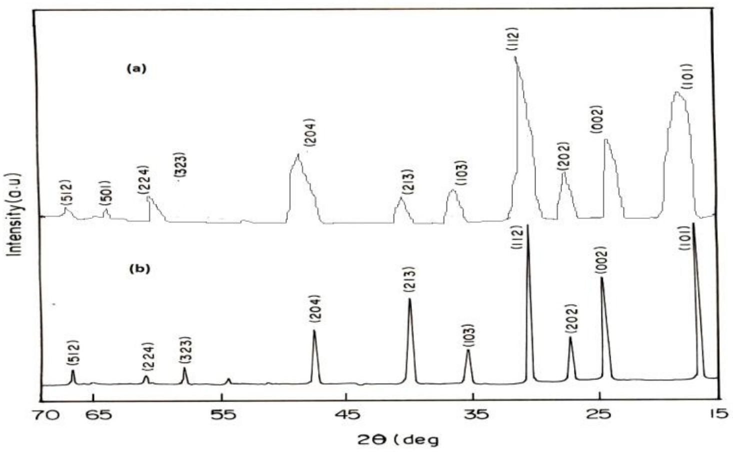

Figure2. *XRD of (a) pure GZS Crystal and (b) Coumarine doped GZS crystal*

It is observed that the reflection lines of the doped GZS crystal correlate well with those observed in the individual parent compound [8, 9] with a slight shift in the Bragg angle. The crystallinity of the grown sample was confirmed by X-ray diffraction analysis.

2.3.2. UV-Visible Studies

UV-visible spectral studies The UV-visible spectral studies of grown crystals were carried out using Shimadzu 1601UV-V spectrophotometer. The UV-visible absorbance spectra of Coumarine dye doped Thiourea crystals are shown in figure 3. The absorption spectra reveal that all three crystals have lower cut off wavelengths at around 290nm. The wide transmission in the entire visible region (190nm- 1100nm) enables it be a potential candidate for optoelectronics applications. It shows that, near absorption edge the absorption coefficient increases rapidly with energy.

A transmission spectrum is very important for any NLO materials, because a nonlinear optical material can be of any practical use if it has a wide transparency window. In the present study, we have recorded the UV-Vis NIR transmission spectrum in the range of 190nm-1000nm is shown in figure 3 and the instrument used in the analysis is LAMBDA-35 UV-Vis spectrophotometer. From the spectrum, it is seen that the crystal has a lower cut-off wavelength of 384nm. The spectrum further indicates that the crystal has a wide optical window from 385nm to 1000nm. The crystal is transparent in the visible and infrared spectral regions. Optical transmittance of about 100% is observed for 1.5mm plates of glycine zinc sulphate crystals and is sufficiently good for SHG [7].

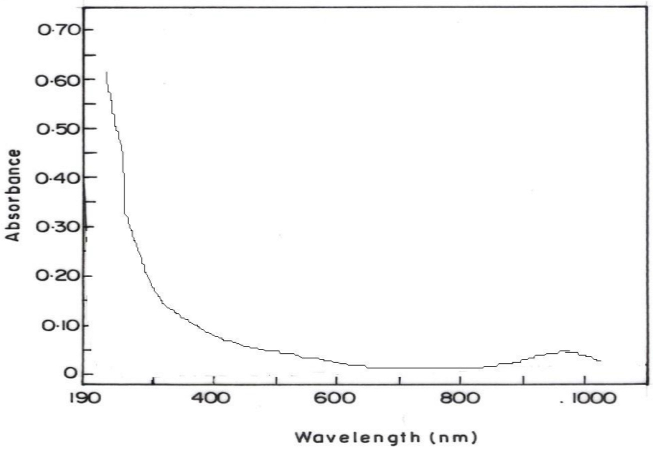

Figure3. *Absorbance spectra of Coumarine dye doped Thiourea crystal*

2.3.3. FTIR Studies

The FTIR [Fig.4] of all of them were recorded from solid phase samples on a bruker IFS 66V model spectrophotometer 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 $2cm^{-1}$. The IR spectra were also recorded on Shimadzu–800, FTIR spectrometer series of Japan in the region 400 – 4000 cm^{-1}. The frequencies [10-12] for all sharp bands are accurate to ± 1 $cm^{-1.}$ The observed spectra of single and doped Thiourea shown in Fig. 2

The FTIR spectral analysis for the grown crystal has been recorded in the range 400-4000 cm^{-1} using KBr pellet technique and the resultant spectrum is shown in Fig.6. The carbonyl stretching C=O is found to be near 1083 cm-1.A peak at 2694 cm-1 corresponds to NH2 deformation. The C-N stretching and the O-H stretching bands are found to be near 1125 and 3186 cm-1 respectively. A peak at 2694 cm-1 corresponds to CH2 stretching. The band at 1580cm-1 indicates the presence of symmetric stretching of carboxylate (COO-) ion. It was confirmed that broad envelope positioned in between 2750-3500 cm^{-1} corresponds to symmetric and asymmetric stretching modes of NH_2 grouping of Coumarine coordinated thiourea. The NH and N-C-N stretching vibrations were also seen in these crystals.

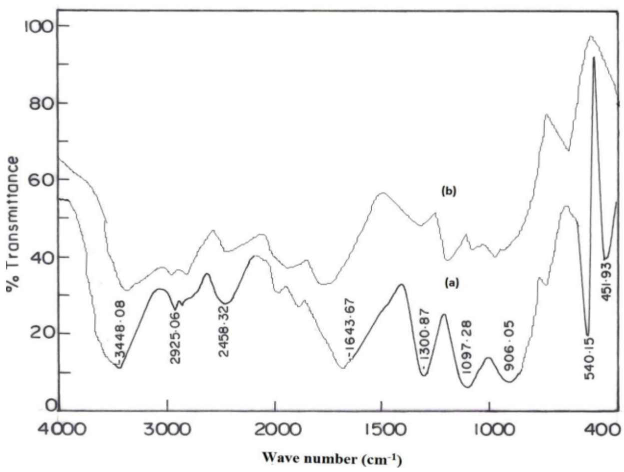

Figure4. *FT-IR spectra of (a) Pure GZS (b) Coumarine doped GZS Crystal*

2.3.4. TGA-DTA Studies

Figure.5 illustrates the differential thermal analysis (DTA) and thermo-gravimetric analysis (TGA) curves for the grown dye doped GZS samples. The DTA curve implies that the material undergoes an irreversible endothermic transition at 200°C where the melting begins. The peak of the endothermic represents the temperature at which the melting terminates which corresponds to its melting point at 210°C. Ideally, the melting point of the trace corresponds to a vertical line. The TG curve of this sample indicates that the sample is stable up to 220°C and above this temperature; the weight loss is not due to self-degradation of doped GZS but merely to its evaporation after it’s melting.

Differential thermogram analysis (DTA) and thermogravimetric analysis (TGA) give information regarding phase transition, water of crystallization and different stages of decomposition of the crystal system. We have carried out simultaneous TGA and DTA for the grown crystals in the temperature range of 30ºC to 1000ºC with a heating rate of 10K / min in the nitrogen atmosphere. The thermogram and differential thermogram are shown in fig.10. The weight loss around 100ºC is due to the presence of water of crystallization in the molecular structure. The endothermic peak at 259ºC is assigned to the melting point of the crystal. The decomposition starts at 259ºC and major weight losses occur which is due to the liberation of volatile substances like carbon mono oxide and ammonia.

Differential thermogram analysis (DTA) and thermogravimetric analysis (TGA) give information regarding phase transition, water of crystallization and different stages of decomposition of the crystal system. We have carried out simultaneous TGA and DTA for the grown crystals in the temperature range of 30ºC to 900ºC with a heating rate of 10K / min in the nitrogen atmosphere. The thermogram and differential thermogram are shown in fig.10. The weight loss around 100ºC is due to the presence of water of crystallization in the molecular structure. The endothermic peak at 160ºC is assigned to the melting point of the crystal. The decomposition starts at 290ºC and major weight losses occur which is due to the liberation of volatile substances like carbon mono oxide and ammonia. The initial mass of the sample was 7.6mg and about 6.6mg of the sample is retained at 900ºC which shows the thermal stability of the crystal system.

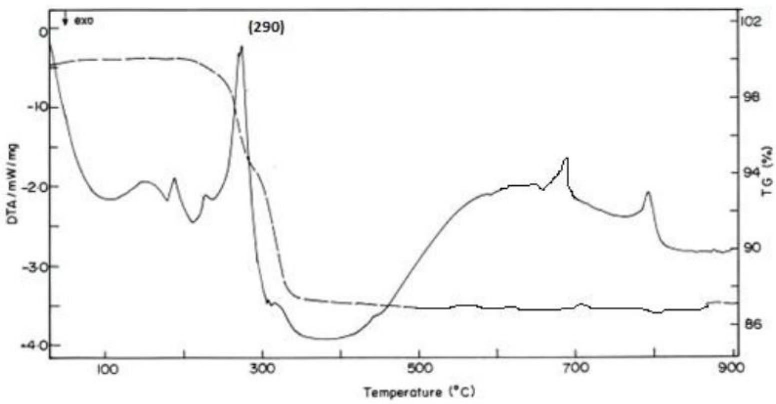

Figure5. *TGA-DTA spectra of Coumarine dye doped GZS crystal*

2.3.5. Vicker's Hardness Test

The mechanical properties of crystals are evaluated by mechanical characteristics. The fastest and simplest type of mechanical testing is hardness measurement. Among the different testing methods, the Vickers hardness test is more commonly used. Microhardness measurements are made using a Leitz microhardness tester fitted with a diamond pyramidal indentor. Single crystal of coumarine doped glycine zinc sulphate crystal is subjected to microhardness on (001) orientation. The applied load is varied from 25 to 200 g for a constant indentation period of 10s. The Vicker's hardness number Hv is calculated using the relation $H_v = 1.8544P/d^2$ Kg/mm^2 where P is the indenter load in kg and d is the diagonal length of the impression in mm [10].

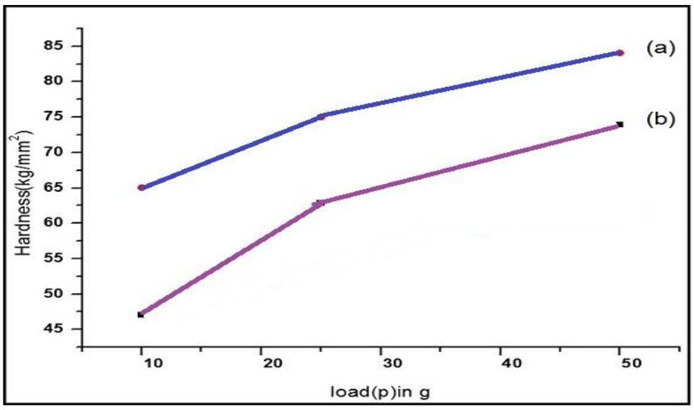

Figure6. *Hardness Studies of (a) Pure (b) Coumarine doped GZS crystal*

The variation of H_v with applied load is shown in Figure 6. It is evident from the plot that the microhardness of the crystal increases on increasing the load. For loads above 200g cracks developed on the surface of the crystal due to the release of internal stress generated locally by indentation.

2.3.6. Dielectric Studies

Dielectric properties are correlated with electro-optic property of the crystals [13]. The dielectric constant is the measure of how easily a material is polarized in an external electric field [14]. The dielectric study on GZS crystal is carried out using the instrument, HIOKI3532-50 LCR HITESTER. A coumarine doped GZS sample having silver coating on opposite faces is placed between the two copper electrodes and thus a parallel plate capacitor is formed [15]. The capacitance is measured in the frequency range of 100Hz to 5MHz. The dielectric constant is calculated using the relation $\varepsilon_r = Cd/A\varepsilon_0$ and is shown in fig8.The dielectric studies were carried out using silver coated samples placed between the two copper electrodes which form a parallel plate capacitor. The capacitance of the sample was noted for the applied frequency that varies from 50 Hz to 5 MHz at different temperatures. Fig.7 shows the plot of dielectric constant (ε_r) versus applied frequency for different temperatures. The applied frequency is represented by logarithmic values in the plot.

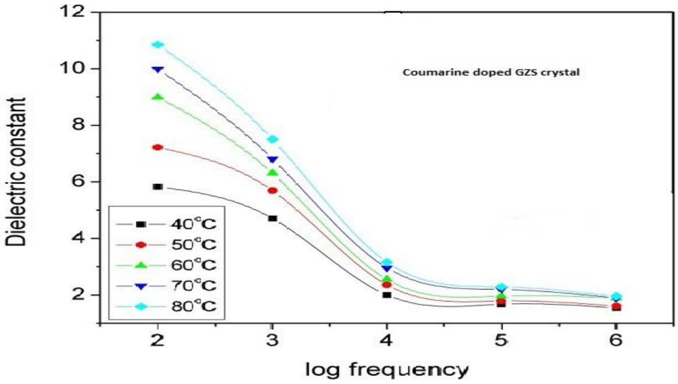

Figure7. *Dielectric Studies of Coumarine doped GZS Crystal*

The dielectric constant decreases with the applied frequency and it is also observed that ε_r increases with increasing temperature (Figure. 7). The very high value of ε_r at low frequencies may be due to the presence of all the four polarizations namely: space charge, orientation, electronic and ionic polarization and its low value at higher frequencies may be due to the loss of significance of these polarizations gradually. The high value of dielectric constant at lower frequencies may be attributed to space charge and ionic polarizations. The low value of dielectric loss at high frequencies suggests that the sample possesses enhanced optical quality with lesser defects and this parameter is of vital importance for NLO applications [13].

2.3.7. SEM Studies

The SEM picture (Fig.8) confirms the formation of a layer on the surface of the crystal due to impurities. The SEM studies reveal that the Coumarine present in the solution creates a surface layer, which prevents the entry of impurities and thereby it helps to grow the crystal with high crystalline quality.

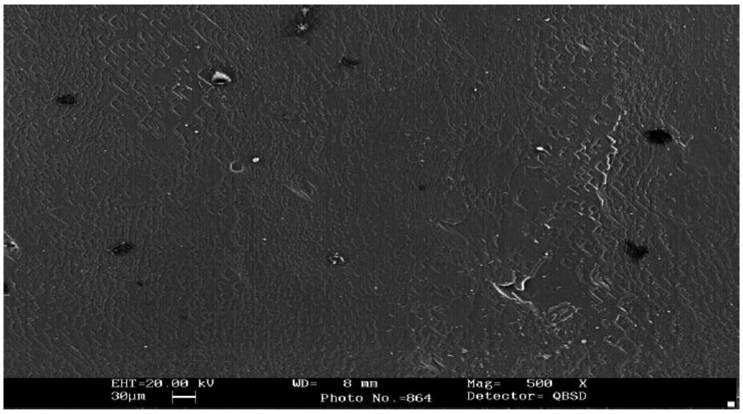

Figure8. *SEM photograph of Coumarine doped GZS crystal (After irradiation)*

The crystal surface morphology of pure and Li+ ion irradiated GZS sample was investigated by SEM and it is shown in Figure 8. It was observed that appears smooth though it has pots and microcrystal on the surface. These inclusions are formed during the crystal growth and they are influenced by the growth conditions.

2.3.8. NLO Properties

Semi organic NLO crystals are particularly attractive for high-speed photonics and THz wave applications. Their NLO figures of merit can be of orders of magnitude higher compared to inorganics, and their long-term orientation and photochemical stability orders of magnitude better as in conventional electro optic polymers. The major challenge for organic NLO crystals remains the micro structuring for VLSI photonics. In the last few years there have been several promising structuring techniques developed for the highly NLO semiorganic crystal-GZS, which open a wide spectrum of new possibilities and functionalities in guided wave photonic technology. Thus, the optical, NLO and thermal properties of the crystal indicate the suitability of this crystal for photonics device fabrication.

In order to confirm the NLO property the coumarine doped GZS crystal has been tested using the Nd-YAG laser. Nd:YAG laser using the first harmonics output of 1064 nm with pulse width of 8 ns and repetition rate10 Hz was passed through the sample. The second harmonics signal, generated in the crystal was confirmed to form the emission of green radiation by the crystal. It shows that Coumarine doped GZS crystals have higher efficiency. It was observed that the irradiation process enhance the NLO property of dye doped GZS crystals.

3. Results and Discussions

We have grown single crystals of GZS and organic dyes doped GZS and characterized them by employing FT-IR and X-Ray diffraction methods. The doped crystals show good second harmonic generation efficiency. There is a different class of non-linear optical materials, which possess important optoelectronic properties. However, to fabricate optical devices using these materials, a detailed study of ion induced stoichiometric and structural changes occurring in them are necessary. Most irradiation studies in the hydrogen bonded ferroelectrics have been concentrated on the transient defects induced by ionizing radiations such as X-ray and 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. In this paper, it has been shown that irradiation modifies the optical properties of GZS crystal [15-16]. Li+ irradiation leads to the development of a well-defined surface H peak. The depletion of hydrogen from the GZS sample in terms of the possible bond-breaking mechanism occurs. Due to beam interaction, an electron moves to the conduction band leaving behind the free hole, which can get self–trapped and configurationally changes occurring in the neighboring structural units.

The irradiation determines diffusion of the dyes uniformly in the crystal. The sharpness of the endothermic peak shows good degree of crystalline of the grown ingot. The endothermic peak at 290°C indicates a phase change from liquid to vapor state as evident from the loss of weight in TG curve. 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. The nature of at electron bonding sequence, the substitution of alternate atoms into the conjugate structure etc. affect the dipole moment and optical susceptibility. The applications of semiorganic molecules are related to two different nonlinear effects exhibited by the molecules. The optical transmittance of the crystal confirms the transparency of the crystal. The band gap energy value (4.25eV) predicted from UV studies confirms the dielectric behavior of the material. Hence, the material is confirmed as a dielectric material to induce polarization for second harmonic generation when a powerful laser beam is incident on the material. The dielectric studies prove that the sample has low dielectric constant and dielectric loss values at high frequency.

4. Conclusion

In this paper, it has been shown that irradiation modify the optical properties of dye doped GZS crystal. 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 neighboring structural units. On the other hand, light beam irradiation effects have been studied. A recent study has been shown that irradiation on a GZS - type crystal, Li^+ irradiations, and leads to the depletion of hydrogen with possible bond-breaking mechanism.

Single crystals of GZS were grown from aqueous solution by slow evaporation technique under room temperature. The grown crystals were characterized by single crystal XRD and it is confirmed that the crystal belongs to the orthorhombic system. The functional group values were predicted by using FTIR analysis. Dielectric measurements were carried to analyze the dielectric constant and dielectric loss at different frequencies and temperatures. Doping organic dyes, the stability of GZS is strong enough and such effect is likely to be reduced. Irradiation effects diffuse the dyes uniformly in the crystal. The nano-islands of dyes in GZS are likely to be dissolved and enhance the nonlinear optical properties of these materials.

ACKNOWLEDGEMENTS

We gratefully acknowledge financial supports from the Department of Science & Technology-Science and Engineering Research Board [DST-SERB-FAST TRACK, PS-20/2009(SR)], New Delhi, India.

REFERENCES

[1] J. Podder, Journal of Crystal Growth 237-239, 70 (2002).

[2] Sonal S .Gupte, Ranjit D.Pradhan, J.Appl.Phys. 91, 3125 (2002)

[3] Shukin Lin, Liting Li, J. Cryst. Growth 249, 341 (2003).

[4] K. Muthu, S.P. Meenakshisundaram, J. Phy. and Chem. of Solids 73, 1146 (2012).

[5] J. Thomas Joseph Prakash, M. Lawrence, Int. J. of Comp. Appl. 8, 37 (2010).

[6] N.R. Dhumane, S.S. Hussaini, V.G. Dongre, M.D. Shirsat, Opt. Mat. 31, 328 (2008). P. Ramasamy, Mat. Chem.Phys. 82, 273 (2003)

[7] H. V.Alexandru, S. Antohe, J. Crystal Growth 258, 149 (2003).

[8] P. Angeli Mary and S. Dhanuskodi, Cryst. Res. Technol. 36, 1231 (2001).

[9] R. Mohan Kumar, D. Rajan Babu, D. Jayaraman, R. Jayavel, and K. Kitamura, J. Cryst. Growth 275.

[10] Tiffany N.Thomas,Terry A Land, Michael Johnson, William H Casey, Journal of Colloid and Interface Science 280, 18 (2004).

[11] G. Bhagavannarayana, S.K. Kushwaha, S. Parthiban, S. Meenakshisundaram, J. Cryst.Growth 311, 960 (2009).

[12] M. Lawrence, Thomas Joseph Prakash, J. Spectrochimica Acta Part A 91, 30 (2012).

[13] G. Pasupathi, P. Philominathan, Mod. Phys. Lett. B 23, 3035 (2009).

[14] G. Madhurambal, B. Ravindran, M. Mariappan, S.C. Mojumdar, J. Therm. Anal Calorim. 108, 905 (2012).

[15] D. Jayalakshmi, J. Kumar, Eur. Phys. J. Appl. Phy. 41, 69 (2008).

[16] P.M. Ushasree, R. Jayavel, P. Ramasamy, Mat. Sc. Eng. B 65, 153 (1999).

[17] H.O. Marcy, L.F. Warren, M.S. Webb, C.A. Ebbers, S.P. Velsko, G.C. Kennedy, and G.C. Catella, Appl. Opt. 31, 5051 (1992).

[18] H. F.Robey, J.Crystal Growth 259, 388 (2003).