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Dielectric and mechanical properties of TGS-KDP mixed crystals

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Abstract

The high purity Analytical Reagent (AR) grade Glycine (CH_2NH_2COOH) and concentrated Sulphuric acid (H_2SO_4) were taken in the molar ratio 3:1 for the synthesis of Triglycine sulphate (TGS) respectively. The synthesized pure TGS is mixed with KDP in the molar ratio (9:1), (8:2), (7:3) and by slow evaporation technique the crystals were grown at room temperature. The Dielectric studies were performed using a LCR meter for the grown crystals. The presence of space charge polarization is confirmed by Dielectric studies. Vickers micro hardness measurement of the grown crystals reveals that hardness increases with load. The log p versus log d were plotted and work hardening co-efficient or Meyer indices (n) is determined. The functional groups are identified by Raman analysis.

Keywords: Crystal growth, Raman Analysis, Mechanical properties, Dielectric properties.

Introduction

Triglycine Sulphate (TGS) crystals has many applications in the technological field of radiation monitoring, astronomical telescopes and earth exploration at room-temperature. At Curie temperature that is $T_C = 49^0C$, TGS undergoes a second-order ferroelectric phase transition, since spontaneous Polarization exists in ferroelectric and pyroelectric materials. However, by applying the electric field to the ferroelectric materials reverses the polarity[1-4]. They are similar to ferromagnetic materials in that they exhibit hysteresis loops. Due to low dielectric constant, high pyroelectric co-efficient and high figure of merit, this material has found various applications in the field of development and fabrication of infrared detectors. Many researchers have studied various aspects of TGS crystals such as its growth rate, pyroelectric, structural modification, mechanical, ferroelectric and optical properties. TGS has a tendency to depole, which can be prevented by suitably mixing optically active molecules in the glycine site of TGS.

This paper describes the crystal growth, Dielectric studies, Mechanical properties and Raman analysis of Triglycine sulphate (TGS) mixed with Potassium dihydrogen Orthophosphate (KDP) in the molar ratio 9:1, 8:2 and 7:3 grown by technique of slow evaporation. The quality and performance of the crystals after mixing KDP to the TGS are also analyzed. The results of the TGS mixed with KDP crystals are compared with the pure TGS crystals.

Materials and methods

Synthesis and crystal growth: The high purity Analytical Reagent (AR) grade Glycine (CH_2NH_2COOH) and concentrated Sulphuric acid (H_2SO_4) were taken in the molar ratio 3:1 for the synthesis of Triglycine sulphate (TGS) as shown in the reaction.

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

The needed amount of concentrated sulfuric acid was diluted using triple distilled water. Then for the diluted sulfuric acid the known amount of glycine was added and dissolved. The glycine solution was slightly heated and dried for few days until the salt gets crystallized. The synthesized pure TGS is mixed with AR Grade Potassium dihydrogen Orthophosphate (KDP) in the molar ratio (9:1), (8:2) and (7:3) using triple distilled water separately in the three glass beakers.

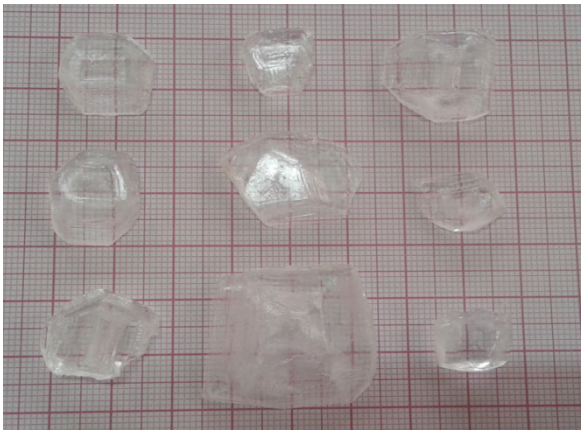

Figure-1: Photograph of Pure TGS single crystals.

The mixed compound is stirred continuously using a magnetic stirrer for 2-3 hours. The completely dissolved solution was filtered using micro filter paper and poured into separate petridish and allowed to evaporate slowly at room temperature.

After a period of 30 days large-size single crystals of optically good quality were obtained. The crystals grown by slow evaporation technique were found to be very stable and transparent. The grown crystals are shown in the Figure 1-4.

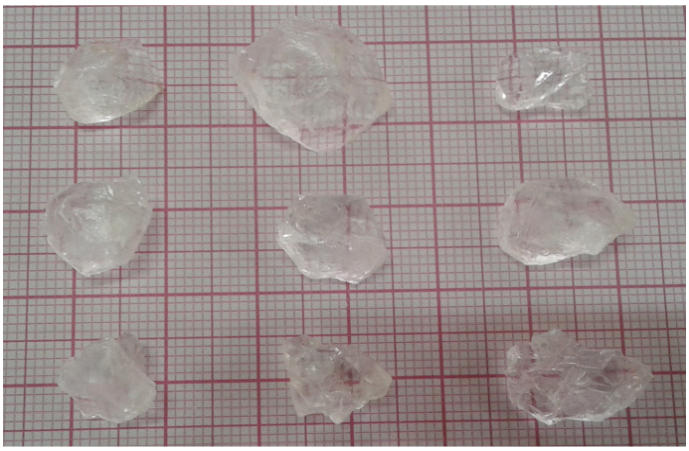

Figure-2: Photograph of TGS:KDP(9:1)single crystals.

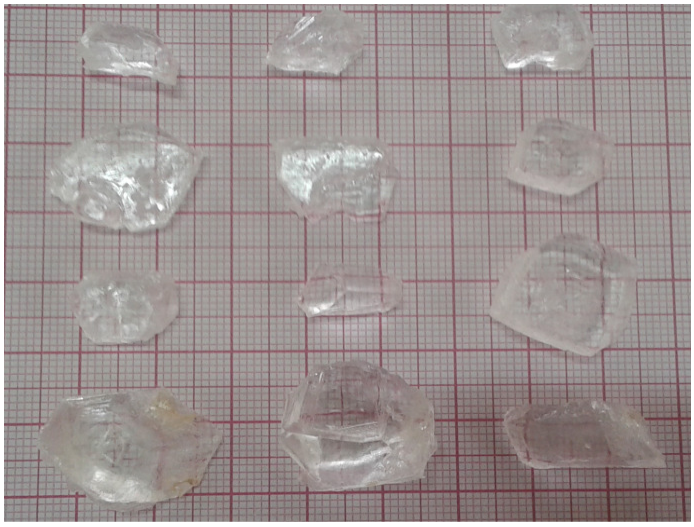

Figure-3: Photograph of TGS:KDP(8:2)single crystals.

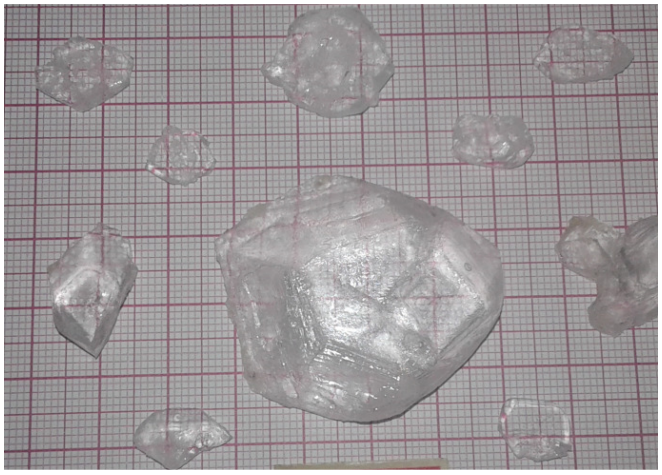

Figure-4: Photograph of TGS:KDP(7:3)single crystals.

Results and discussion

Dielectric studies: Dielectric studies were performed for the grown crystals at various frequencies using LCR meter HEWLETT-PACKARD 4275A model. The crystals of pure and TGS mixed KDP in the molar ratio 9:1, 8:2 and 7:3 are finely cut and polished. And then the grown crystals were coated by air-drying silver paste to make a contact with the electrodes on both the sides. After coating the crystals acts like a capacitor plate. The dielectric constant (ε) and dielectric loss (tanδ) were calculated using the relations (1) and (2).

$$\varepsilon = \frac{Ct}{A\varepsilon_0} \quad (1)$$

$$\tan\delta = D\varepsilon \quad (2)$$

In the above relations C is called the capacitance, t is the thickness, A is the area of the grown crystal in contact with the electrode, ε_o is the permittivity of free space and D is the loss co-efficient respectively.

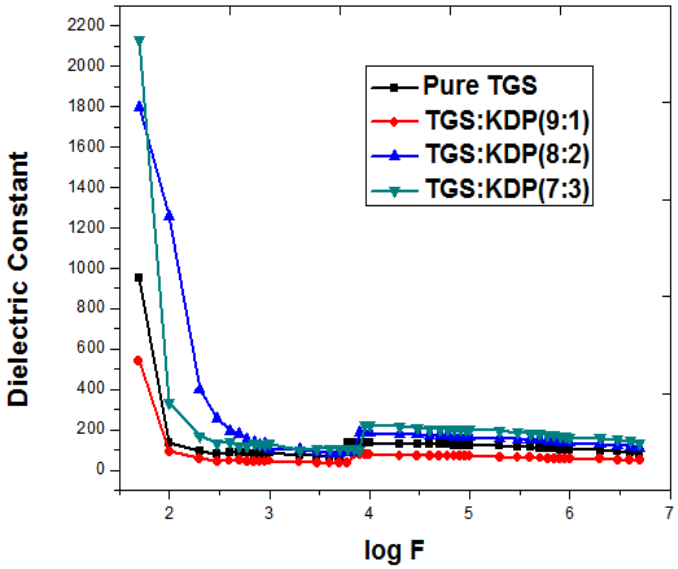

Figure-5: Plot of log frequency versus dielectric constant for the grown crystals.

At normal temperature the variations of dielectric constant (ε) and dielectric loss (tanδ) is measured for pure TGS and TGS mixed KDP in the molar ratio 9:1, 8:2 and 7:3 crystals and are shown in Figure-5 and 6. From the Figure it is seen that the dielectric constant (ε) is maximum at 100 Hz and it gradually decreases as the frequency increases. At high frequencies due to the inertia of the ions and molecules, the orientation and ionic contributions of polarization decreases. The dielectric loss (tan δ) is directly proportional to the product of dielectric constant (ε) and loss co-efficient (D) that makes them to decrease. Tanδ the dielectric loss was found to be initially maximum and then it decreases gradually as frequency increases and later it becomes almost a constant over a range of frequencies.

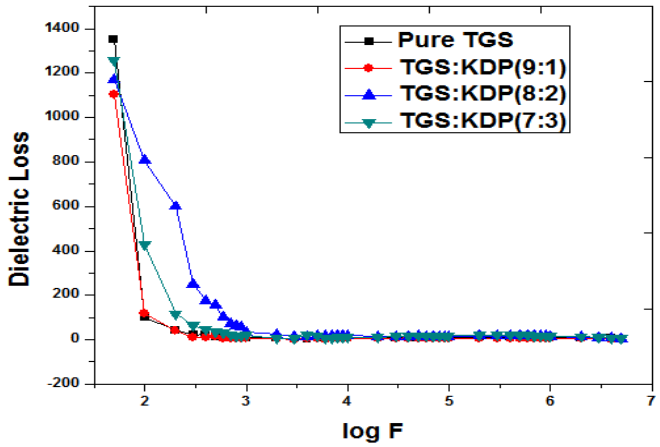

Figure-6: Plot of log frequency versus dielectric loss for the grown crystals.

The a.c. conductivity depends on the negative charges which happens due to leakage currents. This movement of negative charges results in polarization in the solid state dielectrics. But at higher temperature some of the negative ions come out from the crystal lattice sites due to ionic conduction[5].

At low frequencies, Space charge polarization will be more, where as it is absent at high frequencies. Due to the uniform motion of ions in the variation of field, at high frequency the space charge polarization decreases. The conductivity and resistivity variation is plotted along with the frequency for the grown crystals are shown in Figure-7 and 8. The relation used for calculating the a.c. resistivity and a.c. conductivity are given by (3 and 4).

$$\rho = \frac{A}{2\pi f C t} \quad (3)$$

$$\sigma\rho = \frac{1}{\rho} \quad (4)$$

From the above relation A corresponds to the area of the crystal, f is the frequency of the applied field, C is called the capacitance and t is the thickness of the grown crystal. From the graph it is observed that a.c. resistivity decreases very fast as frequency increases. But in a.c. conductivity studies, we see the reverse operation that is when frequency is increased for the grown crystals the a.c. conductivity also increases, which shows a normal dielectric behavior[6].

Raman analysis: The Raman spectra of grown crystals were recorded for (101) planes at room temperature in the wave number range of 200 to 2000 cm-1. Raman spectra in the range of 200 to 2000 cm-1 is shown in Figure-9. The spectra of pure TGS, TGS:KDP (9:1), TGS:KDP (8:2) and TGS:KDP (7:3) crystals contain the internal modes of vibrations at 974 cm^{-1} (ν1), 575 cm^{-1} (ν2), 663 cm^{-1} (ν3), 868 cm^{-1} (ν4), 890cm^{-1} (ν5), 1309cm^{-1} (ν6), 1435cm^{-1} (ν7), and 1605 cm^{-1} (ν8). The peaks with very small intensity are related to the vibrations of crystal lattices by the emission or absorption of phonons. Using the energy time uncertainty formula, the Phonon life time (τ) can be calculated given by relation (5).

$$\frac{1}{\tau} = \frac{\triangle E}{h/2\pi} = 2\pi\,\Gamma \quad (5)$$

From the above relation it is seen that ΔE is the energy of the phonon in the uncertainty mode, h is the Planck constant, and Γ is the Full width half maximum (FWHM) of the Raman peaks. The phonon life time is an addition of two characteristic decay time that is an harmonic decay of the phonon (τ_A) and disturbance of translational uniformity of the crystals due to the existence of defects, impurities and isotropic fluctuations (τ_1).

$$\left(\frac{1}{\tau} = \frac{1}{\tau_A} + \frac{1}{\tau_1}\right)$$

The calculated values of phonon life time and the vibrational frequencies corresponding to the band assignments of pure TGS and TGS: KDP mixed crystals are listed in Table-1.

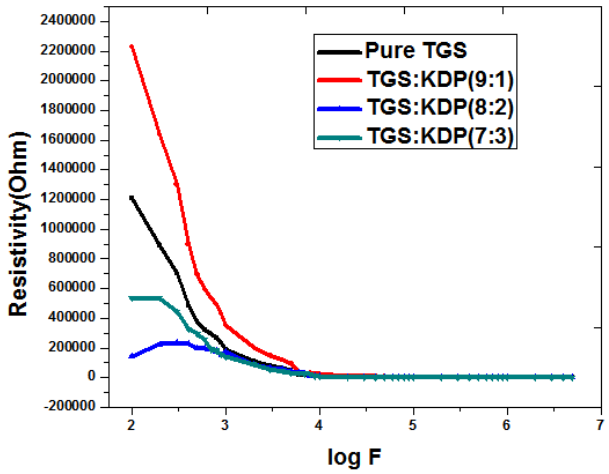

Figure-7: Plot of log frequency versus AC resistivity for the grown crystals.

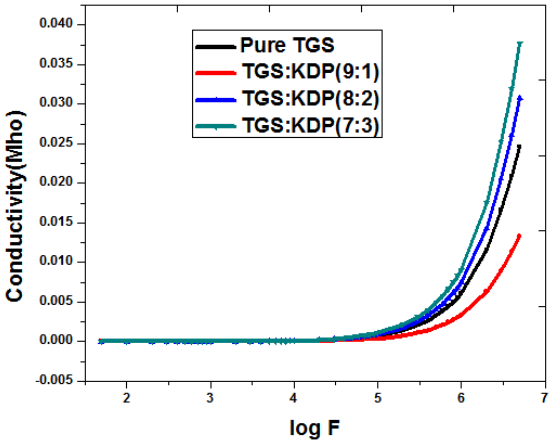

Figure-8: Plot of AC conductivity versus log frequency for the grown crystals.

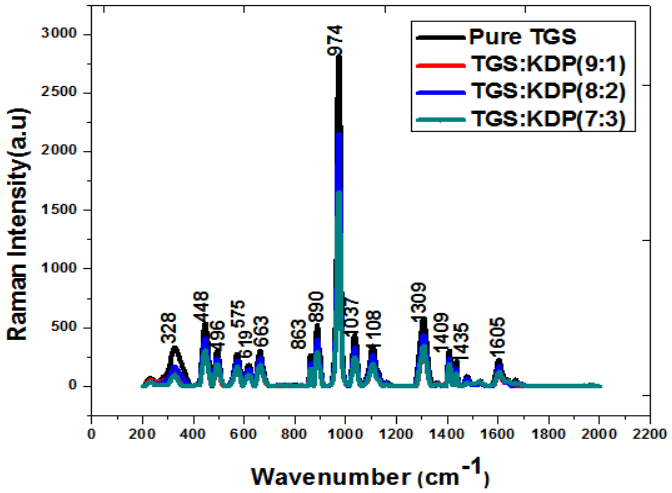

Figure-9: FT-Raman Spectrum of grown crystals.

Table-1: Phonon life time and symmetry of grown crystals.

Reference (cm^{-1})	FWHM (Γ) cm^{-1}	Phonon life time (τ) μs	Symmetry
575	22.17	71.78	PO_4 Stretching
619	23.77	66.95	PO_4 Stretching
663	24.67	64.51	PO_4 Stretching
863	12.27	129.71	P-OH deformation/ K-O Stretching
890	19.21	82.85	HO-P-OH bending
974	18.42	86.40	O=P-OH bending
1037	19.41	81.99	P-O-H symmetric stretching
1108	26.23	60.67	P-O-H symmetric stretching
1309	33.23	47.89	CH_2 bending, P=O symmetric stretching
1409	16.68	95.41	O-H Stretching
1435	13.60	117.03	O-H Stretching
1605	25.78	61.73	O-P-OH symmetric stretching

Micro hardness studies: Vickers micro hardness test is used to study the mechanical properties of the grown crystals. The grown crystals of pure and TGS:KDP mixed crystals of different molar ratio with smooth surfaces was selected for micro hardness studies using Future Tech Micro hardness tester FM-800. Crystals hardness generally depends on the resistance that is offered by a solid in the displacement of crystal lattice structure, but practically this is caused by indentation[7,8]. Mechanical stress is applied by the indenter, then the dislocations are formed at the area of indentation. The Vickers hardness was measured for the different loads applied to the indentation area of the surface. The applied loads are 10, 25, 50 and 100g for which Indentations were performed using Vickers micro hardness indenter. For each load two or three indentations were performed and the mean value was taken for the diagonal length and substituted in the relation (6) to calculate the micro hardness of the crystals.

$$Hv = \frac{1.8544p}{d^2} \quad (6)$$

From the above relation it is seen that p is the different load applied in gram and d is the diagonal length of the indentation. The graph of applied load in gm versus the Vickers micro hardness H_V in kg/mm^2 was plotted for pure and TGS: KDP mixed crystals of different molar ratio as shown in Figure-10. The graph shows that from 10 to 100 gm the hardness value increases, above that load the cracks were formed at the indentation mark, due to the discharge of stress developed internally. The addition of KDP to TGS crystal has improved the crystals hardness value and thus confirming the crystalline perfection.

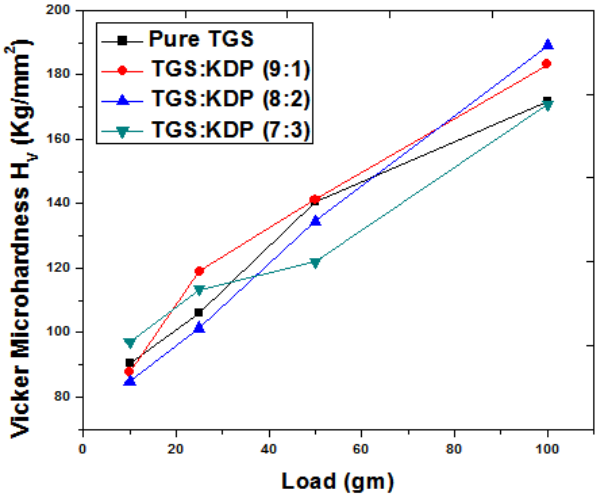

Figure-10: Plot of micro hardness study for grown crystals.

The log d versus log p are also plotted as shown in Figure-11. The graph shows nearly a straight line from which the slope of the best fitted points are obtained. The value of the slope gives the work hardening co-efficient or Meyer indices (n) and are shown in Table-2. The Meyer's law[9] is expressed in relation (7).

$$P = Kd^n \quad (7)$$

Where: K is the constant value of the material. Hanneman and Onitsch have showed that Meyer indices 'n' value will be within 1.0 and 1.6 for hard material and more than 1.6 for soft material[9]. The obtained values of 'n' in our present work are found to be greater than 1.6, which indicates that all our grown crystals belongs to the category of soft material.

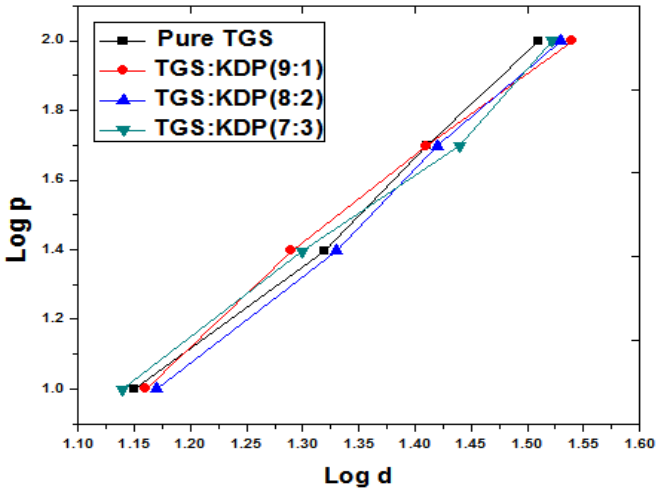

Figure-11: log d versus log p plot of grown crystals.

Table-2: Work Hardening Co-efficient of grown crystals.

Sample	Work Hardening Co-efficient (n)
Pure TGS	2.78
TGS:KDP (9:1)	2.62
TGS:KDP (8:2)	3.19
TGS:KDP (7:3)	2.54

Conclusion

Optically transparent good quality single crystals of pure TGS and TGS-KDP mixed in the molar ratio (9:1), (8:2) and (7:3) were grown by the technique of slow evaporation at room temperature. The existence of distinctive functional groups was approved by Raman spectrum. The dielectric studies show that the grown crystal has low dielectric constant and low dielectric loss. The Vickers micro hardness studies shows that the grown crystals has maximum surface hardness and belongs to soft material category having low yield strength. As the crystal has low dielectric constant, dielectric loss, and maximum surface hardness implies that this crystal can be used as a promising material for optical applications.

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References

1. Banan M., Lal R.B., Batra A.K. (1992) Modified triglycine sulphate (TGS) single crystals for pyroelectric infrared detector applications. *Journal of materials science*, 27(9), 2291-2297.

2. Meera K., Muralidharan R., Santhanaraghavan P., Gopalakrishnan R. and Ramasamy P. (2001). Growth and characterisation of l-cystine doped TGS crystals. *Journal of Crystal Growth*, 226(2), 303-312.

3. Arunmozhi G., Lanceros-Me´ndez S., Matos Gomes E. de (2002), *Materials Letters*, 54, 29-336.

4. Jeyaprakash Manoharan A.J., Joseph John N., Revathi V., Rajendran K.V. and Andavan P.M. (2011). Effect of amino acid doping on the dielectric properties of triglycine sulphate (TGS) crystals. *Indian Journal of Scienceand Technology*, 4(6), 688-691.

5. R. Priya, G. Bhagavannarayana, S. Krishnan and S. Jerome Das (2010), *Archives of Applied Science Research*, 2(4), 111-118.

6. S.Suresh, A. Ramanand, P. Mani and K. Anand (2010). Dielectric characteristion of Benzoyl Glycine crystals. *Archives of Applied Science Research*, 2 (4), 119-127.

7. P. Rajesh, P. Ramasamy, K. Kumar, G. Bhagavannarayana (2010). Effect of cobalt and DL-malic acid on the growth rate, crystalline perfection, optical, mechanical, dielectric, piezoelectric properties and SHG efficiency of ADP single crystals. *Physica B*, 405(10), 2401-2406.

8. Vijayan N., Bhagavannarayana G., Babu Ramesh R., Krishnan Gopala R., Maurya K.K. and Ramasamy P. (2006). A comparative study on solution-and bridgman-grown single crystals of benzimidazole by high-resolution X-ray diffractometry, fourier transform infrared, microhardness, laser damage threshold, and second-harmonic generation measurements *Cryst.Growth Des.*, 6(6), 1542-1546.

9. K. Karan and Gupta S.P. (2005). *Master.Sci.Eng*., A398, 198, (2005).