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Investigation on thermal, functional, dielectric studies of semiorganic bis glycine maleate crystals

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ABSTRACT

A single crystal of bis glycine maleate has been grown from aqueous solution by slow evaporation method by optimizing the growth parameters within a period of 45 days. From the x-ray diffraction, the crystal was found to crystallize in a hexagonal structure with a=7.402 Å, b=7.04 Å, c= 5.48 A and α=β=90 °, γ =120 °. The functional group was confirmed by FTIR analysis. The photoconductivity study confirmed that it is a positive photoconductivity. Thermal studies have also been studied and by investigating to the second harmonic generation it is confirmed to be a non-linear crystal. The results have been discussed in detail.

Keywords: Thermal NLO, dielectric loss, dielectric constant.

INTRODUCTION

Since 1961, when the Nonlinear Optical (NLO) Phenomenon was observed for the first time, NLO frequency conversion materials have played more and more important role in many fields, such as laser technology, optical communication, optical data storage etc. [1]. In the context of NLO, organic materials have advantages such as large NLO coefficients and structural diversity or flexibility, compared to the inorganic counterparts [2]. They also have some inherent drawbacks, for example, poor physico- chemical stability and low mechanical strength. As a result, the quest for new frequency conversion materials is presently concentrated on semi-organic crystals due to their large nonlinearity, high resistance to laser induced damage, low angular sensitivity and good mechanical hardness [3–5]. Crystals of amino acid family have been grown and studied by several researchers for their excellent nonlinear optical (NLO) properties [6-8]. It is known that glycine, the simplest amino acid, exhibits three different polymeric forms viz. α-glycine, β-glycine and γ-glycine. Among the three forms, γ glycine exhibits strong piezo-electric and NLO effect [9-10]. Unlike other amino acids, glycine is the simplest amino acid and has no asymmetric carbon atom and is optically inactive. Since the glycine molecule can exist in a zwitterion form, it is capable of forming compounds with anionic, cationic and neutral chemical compounds. Thus, a large variety of glycine coordinated compounds can be formed.

However, only those complexes of glycine, which crystallizes in a noncentrosymmetric structure, are expected to exhibit nonlinear optical second harmonic generation [11-13]. Glycine and its methylated analogues form complexes with mineral acids exhibiting interesting physical properties like ferroelastic, ferroelectric or antiferroelectric behaviour. It has been reported that amino acid dopants increased the thermal stability, optical transparency and second harmonic generation efficiency of KDP single crystals [14]. There has been a large amount of research work done to induce the molecules into non-centrosymmetric environments with high value of β [15]. The assembly of non-centrosymmetric segregation of Centro-symmetric molecules can be achieved through various physical and chemical methods [16]. Semi-organics include organic–inorganic salts and metal– organic coordination compounds [17]. Among the organic materials amino acids constitute a family in which glycine is the simplest of all the amino acids. It has been reported that some complexes of amino acids with simple inorganic salt may exhibit ferroelectric

properties [18-20]. Some complexes of glycine with CaCl2 [21], BaCl2 [22], H2SO4 [23] and CoBr2 [24] form single crystals, but none of these are reported to have nonlinear optical property. Single crystals of glycine sodium nitrate [25], glycine lithium sulphate [26] and benzoyl glycine [27] showed non-centrosymmetry and their quadratic nonlinear coefficients were examined.

The crystals of centrosymmetric a glycine in its pure form show SHG upon occlusion of 'guest' molecules [28]. Organic nonlinear optical (NLO) materials formed from amino acids have potential application in second harmonic generation (SHG), optical storage, optical communication, photonics, electro-optic modulation, optical parametric amplifiers, optical image processing, optical bistable devices, optical modulators, optical switches etc., [29]. The single crystals of γ-glycine in the presence of small amount of sodium nitrate, lithium nitrate, strontium chloride, potassium, potassium chloride, potassium bromide, phosphoric acid, ammonium acetate, ammonium nitrate, sodium acetate, hydrofluoric acid, ammonium chloride [30-40] are reported as good NLO material.

In the present investigation, the growth aspect of BGM is discussed. The grown crystal has been subjected to XRD, FTIR, Thermal, Photoconductivity, Dielectric studies and also Second Harmonic property has been studied.

1. Synthesis

Analytical grade glycine and maleic acid in the molar ratio 2:1 were taken for the synthesis (Balasubramanian 2010). Calculated amount of glycine was first dissolved in 10% of alkaline medium ammonium hydroxide solution. Then, maleic acid was added to the solution slowly. The reaction mechanism of the chemical synthesis is as follows.

$$2(NH_2CH_2COOH) + COOH - CH = CH - COOH$$
$$\rightarrow HOOC - H_2C - NH_3COO - CH + CH - COO - NH_3 - CH_2 - COOH$$

Synthesized salt of BGM was obtained from the solution by evaporating the solvent and collecting the precipitate formed at the bottom of the container with the solution. The purity of the synthesized salt was increased by successive recrystallization process.

1.1 Solubility

The synthesized salt was used to measure the solubility of BGM in water. A 250 ml glass beaker filled with 100ml deionized water was placed inside a constant temperature bath whose temperature was set at 30°C. The solvent was completely evaporated by warming the solution slightly in room temperature.

1.2 Growth of SPPD

The supersaturated solution was prepared in accordance with the solubility. Single crystals of Bis-glycine Maleate were grown from their aqueous solution using slow solvent evaporation technique. The solvent of the supersaturated solution was allowed to evaporate

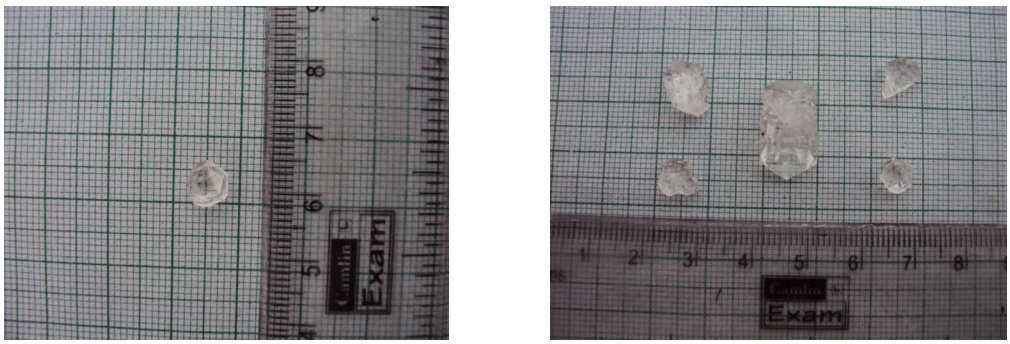

Fig: 3.1 Photographs of grown crystals of BGM

through the perforated lid of the container. Numerous tiny crystals were formed at the bottom of the container due to spontaneous nucleation. The transparent and defect free ones among them were chosen as seeds for growing bulk crystals. By seeding the supersaturated solution and evaporating the solvent good optical quality crystals were harvested after a period of 45-60 days. The photographs of grown crystals of BGM are shown in the Fig (3.1). Ammonium hydroxide was found to be a better solvent for growing single crystals of BGM because of its high solubility and low evaporation rate [41].

2. Characterization

2.1.1 Single Crystal XRD study

The X-ray diffraction data was collected by using an automatic X-ray diffractometer Enraf Nonius CAD4-MV31.The XRD data of the sample are presented in Table (3.1). The X-Ray diffraction study reveals that the crystal belongs to the non-centrosymmetric hexagonal crystal system and the lattice parameters are a= 7.04 Å, b=7.04 Å, c=5.48 Å, and α=γ=90°, β= 120° in good agreement and belongs to the space group P1. This confirms the single crystal nature of BGM.

2.1.2 Powder X -Ray diffraction

Powder X-ray diffraction spectrum was recorded by using an XPERT-PRO diffractometer with Cuk α (1.5406 Å) radiation. The sample was scanned over the range of 2θ=70° at a rate of 10.13 min. The indexed powder XRD pattern of the grown crystal was shown in Fig (3.2). The lattice parameter values have also been calculated. The particle size, dislocation density and strain values were calculated in Table (3.2). It shows the corresponding FWHM value increase towards increase in dislocation density and strain value and decrease in particle size

2.1.3 FT-IR Spectrometer

The infrared spectral analysis is effectively used to understand the chemical bonding and it provides information about molecular structure of the synthesized compound. Each and every chemical compound have their own typical IR spectrum [37,42].FTIR spectrum of the Bis- glycine maleate compound recorded in the wavelength range of 600-4000cm-1 using Bruker IFS 66V FTIR Spectrometer has been shown in the Fig.(3.3).

The broadband in the higher energy region between 3112 and 2601 cm-1 is due to NH3+ stretching vibrations. The band at 2169 cm-1 may be assigned to a combination of the asymmetrical NH3+ bending vibration and the torsional oscillation of the group NH3+.Two overlapped bands at around 1589 and 1491 cm-1 were attributed to the asymmetric and symmetric stretching mode of the COO- group. The peaks around 1439, 1328, 683 and 500 cm-1 has been attributed to CH2 bending, CH2 twisting, COO-bending and COO- rocking respectively. The presence of carboxylate and ammonium ion clearly indicates that the glycine molecule exists in zwitterionic form in γ-glycine crystal. The frequencies of the vibrational mode of the crystal and their assignments are given in Table (3.3).The observed data of γ-glycine were compared with spectral frequencies of standard γ- glycine [43].

Table 3.1: Crystal Data and Structure Refinement Parameters for BGM crystal

Identification code	NPPD
Empirical formula	$HOOC-H_2C-NH_3COO-CH+CH-COO-NH_3-CH_2-COOH$
Crystal system	Hexagonal
Space group	P_1
Unit cell dimensions	a= 7.04 Å b=7.04 Åc=5.48 Å α=γ=90°β= 120 °
Volume	235 $Å^3$

Table: 3.2 Calculated Structural Parameters

S.no	FWHM β (deg)	Particle size D (m)	Dislocation Density δ (Kg/m^3)	Strain Value ε (line $^{-2}/m^{-4}$)
1	0.04	36.9285	0.7332	0.0098
2	0.08	19.723	2.5821	0.01835
3	0.12	12.8272	6.1186	0.0282
4	0.16	9.349	11.4655	0.03873

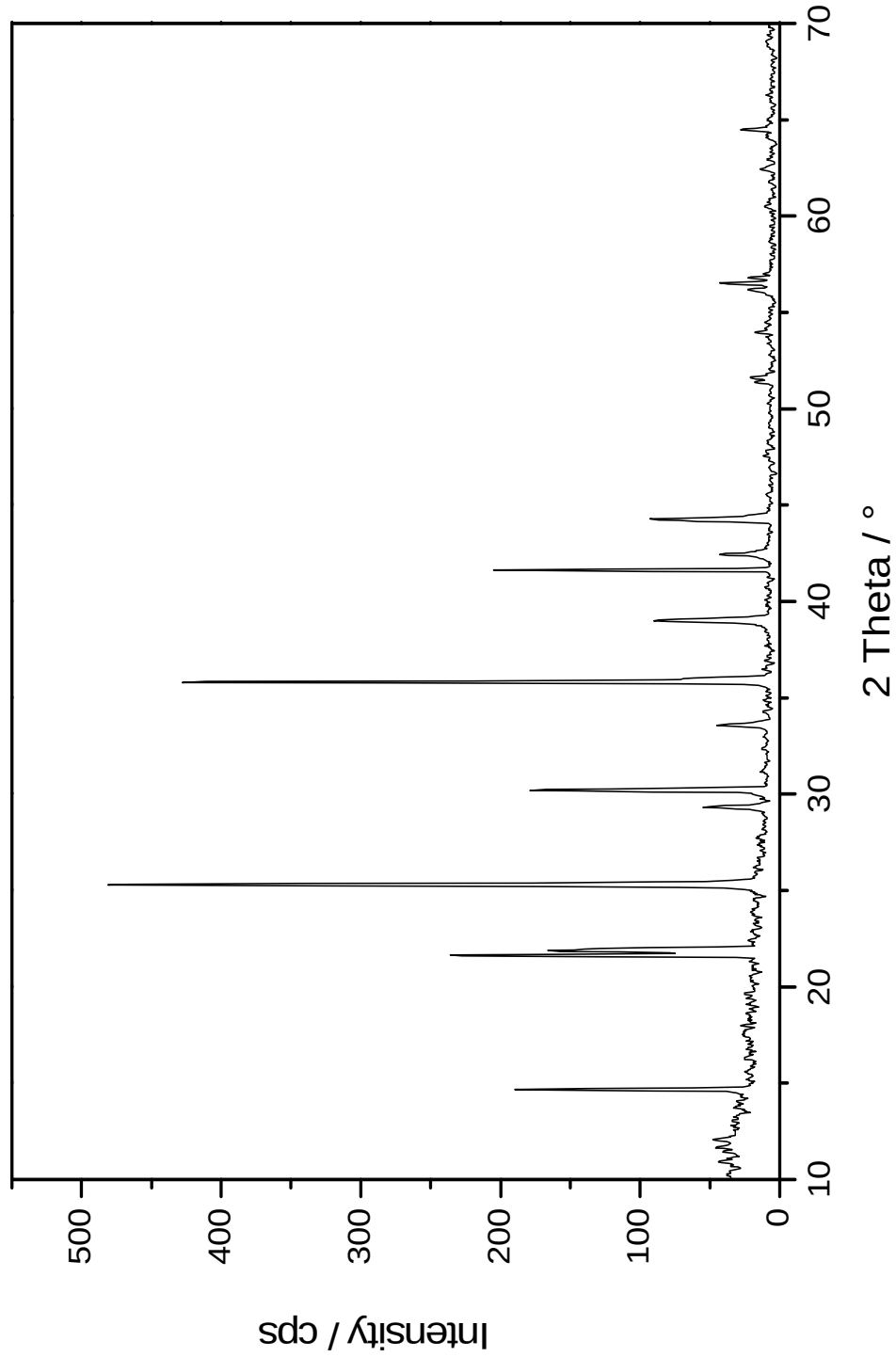

Fig: 3.2Indexed powder XRD pattern of the grown crystal

Table: 3.3 FTIR –frequency assignment for BGM single crystal

Wave Number cm^{-1}	Mode	Assignments
500	-COO	Rocking
606	-COO	Wagging
683	-COO	Bending
886	CCN	Symmetric Stretching
927	CH_2	Rocking
1040	CCN	Asymmetric Stretching
1124	NH3 +	Rocking
1328	CH_2	Twisting
1385	COO-	Symmetric Stretching
1439	CH_2	Bending
1491	COO-	Asymmetric Stretching
1589	COO-	Asymmetric Stretching
2601,3112	NH3 +	Stretching

2.1.4 Photoconductivity study of BGM single crystal

The field dependent photoconductivity of the BGM crystal has been shown in Fig. (3.4). It is observed that the dark current (d) and the photocurrent (p) shows linear response with respect to the applied field and at any instant and the photocurrent was found to be greater than the dark current. Hence, the crystal exhibits positive photoconductivity. As the crystal is possessing high band gap for photon absorption, the applications are extended for soliton wave communication, where the optical pulses propagate within the photonic band gap for large distances without any distortion [44].

2.1.5 Thermal studies

Thermogravimetric and differential thermal analysis gives information regarding phase transition, water of crystallization and different stages of decomposition of the crystal system. The thermogravimetric analysis of BGM crystal is carried out between 20°C and 400°C in the nitrogen atmosphere at a heating rate of 10 K min^{-1} using Perkin-Elmer thermal analyser (STA 409 PC). The obtained spectrum has been shown in Fig (3.5).The weight loss of 17.82% occurred at 196.95°C which was associated with a sharp exothermic peak at the same temperature attributed to the utilization of thermal energy to overcome the valence bonding between the glycine cation and maleate anion that happens in the initial stages of decomposition.

The maleic acid decomposes between the temperatures 190.65°C and 241.12°C. The endothermic peak observed at 261.72° C corresponds to the formation of peptide. Reactions of simplest amino acids induced by heating include the condensation reactions of carboxyl and amino groups leading to the formation of peptide bonds. Further heating results in the liberation of NH3+ above 300°C.

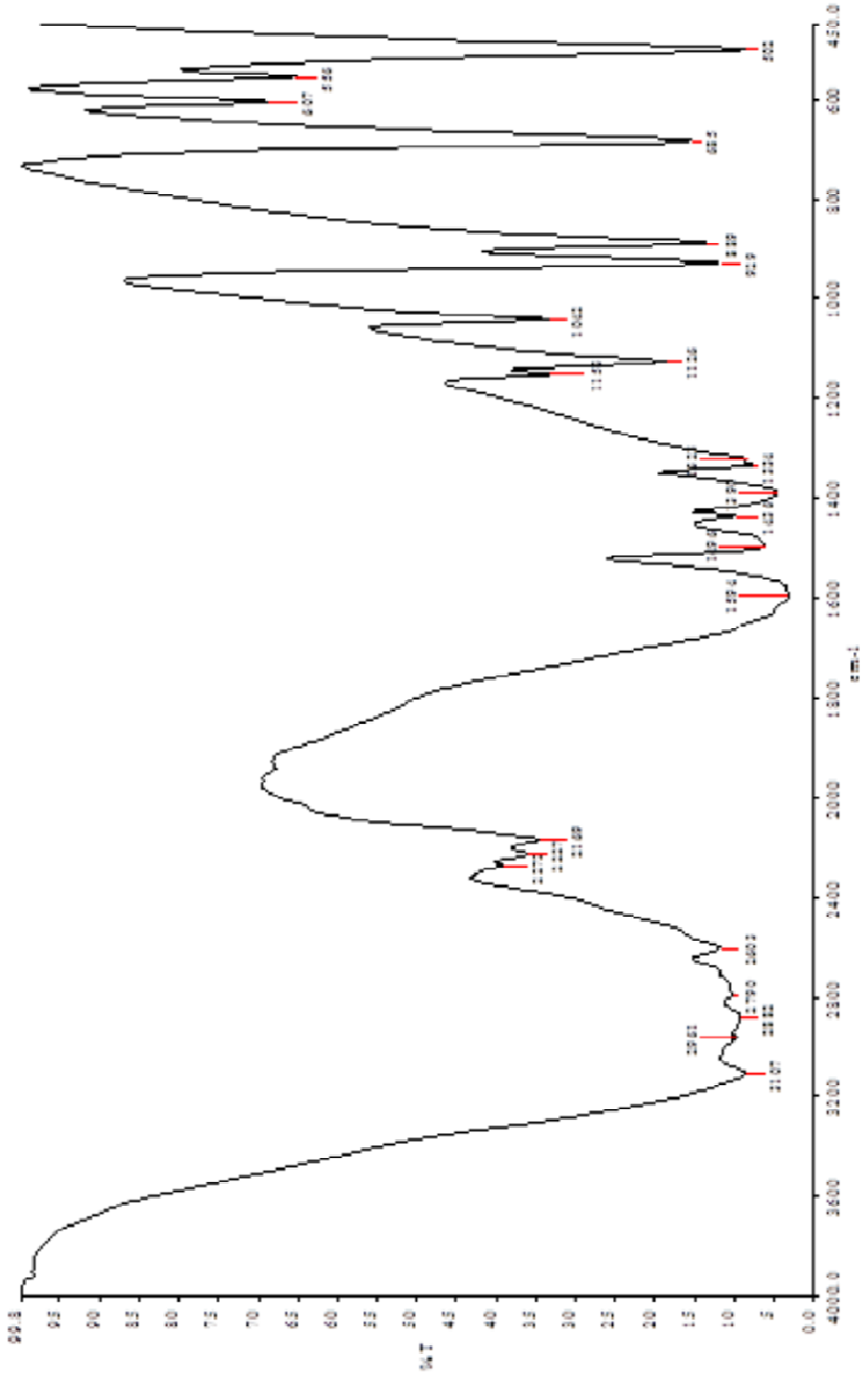

Fig3.3 FTIR Spectrum of BGM Single crystal

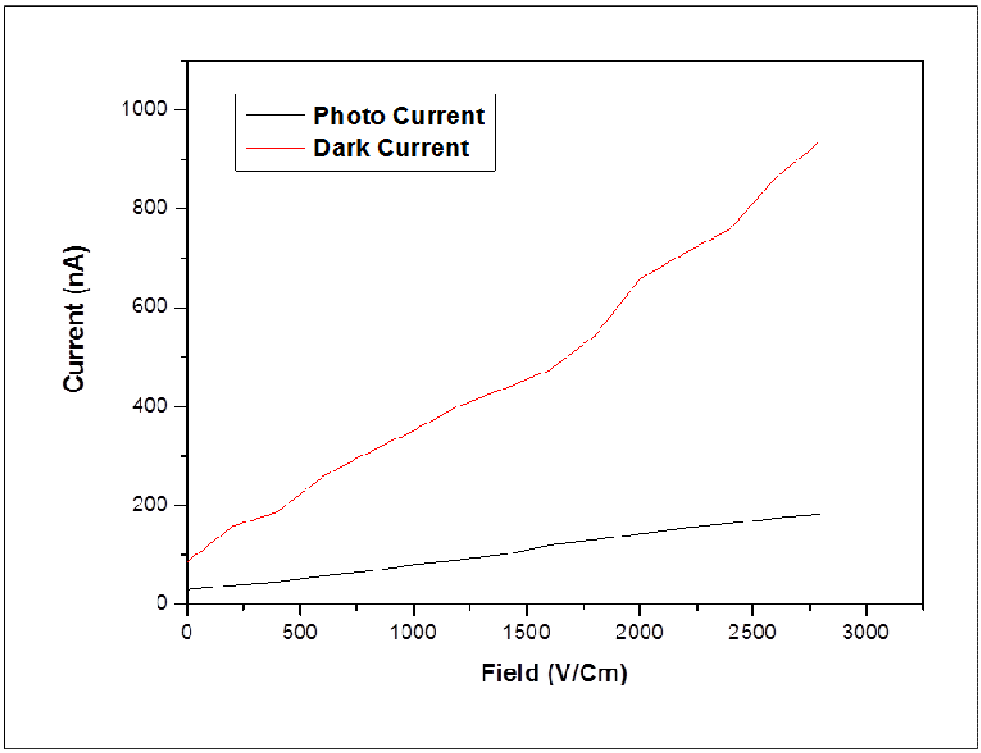

Fig: 3.4 Variation of Microhardness with applied load of BGM single crystal

2.1.6 Dielectric studies on BGM crystal

Good quality single crystal of BGM were cut and polished with a soft tissue paper with fine grade alumina powder.In order to ensure good electrical contact between the crystal and the electrodes, the crystal faces were coated with silver paste. The dielectric measurements were carried out in the frequency range 50–5 MHz and temperature range 313–373K with the help of an impedance analyser, HIOKI3532-50LCRHiTESTER. Fig.3.6(a) shows the plot of dielectric constant as a function of frequency. It has been observed that the dielectric constant decreases with the increase in frequency for all temperatures. The large values of dielectric constant at low frequency enumerates the contribution from all four known sources of polarization namely, electronic, ionic, dipolar and space charge polarization. Space charge polarization was generally active at lower frequencies and high temperatures and be taken the perfection of the crystal. Further, the space charge polarization will reckon on the purity and perfection of the material. Its influence was large at higher temperature and was noticeable in the low-frequency region. The characteristic flow of dielectric loss with high frequency for a given sample was observed from Fig.3.6 (b) suggests that the sample possess good optical quality with lesser defects and this parameter has of vital importance for nonlinear optical applications

The response of dielectric constant with temperature has been shown in Fig.3.6(c)&3.6(d).It was found that dielectric constant gradually increases with the increase of temperature. This indicates the presence of space charge effect in addition to electronic and atomic conduction in the samples.No abrupt changes are observed in the response indicating the absence of any phase transition; this was confirmed by the thermal studies.

The dielectric loss shows the similar behaviour as dielectric constant. Maximum of loss tangent increases with the increasing frequency.

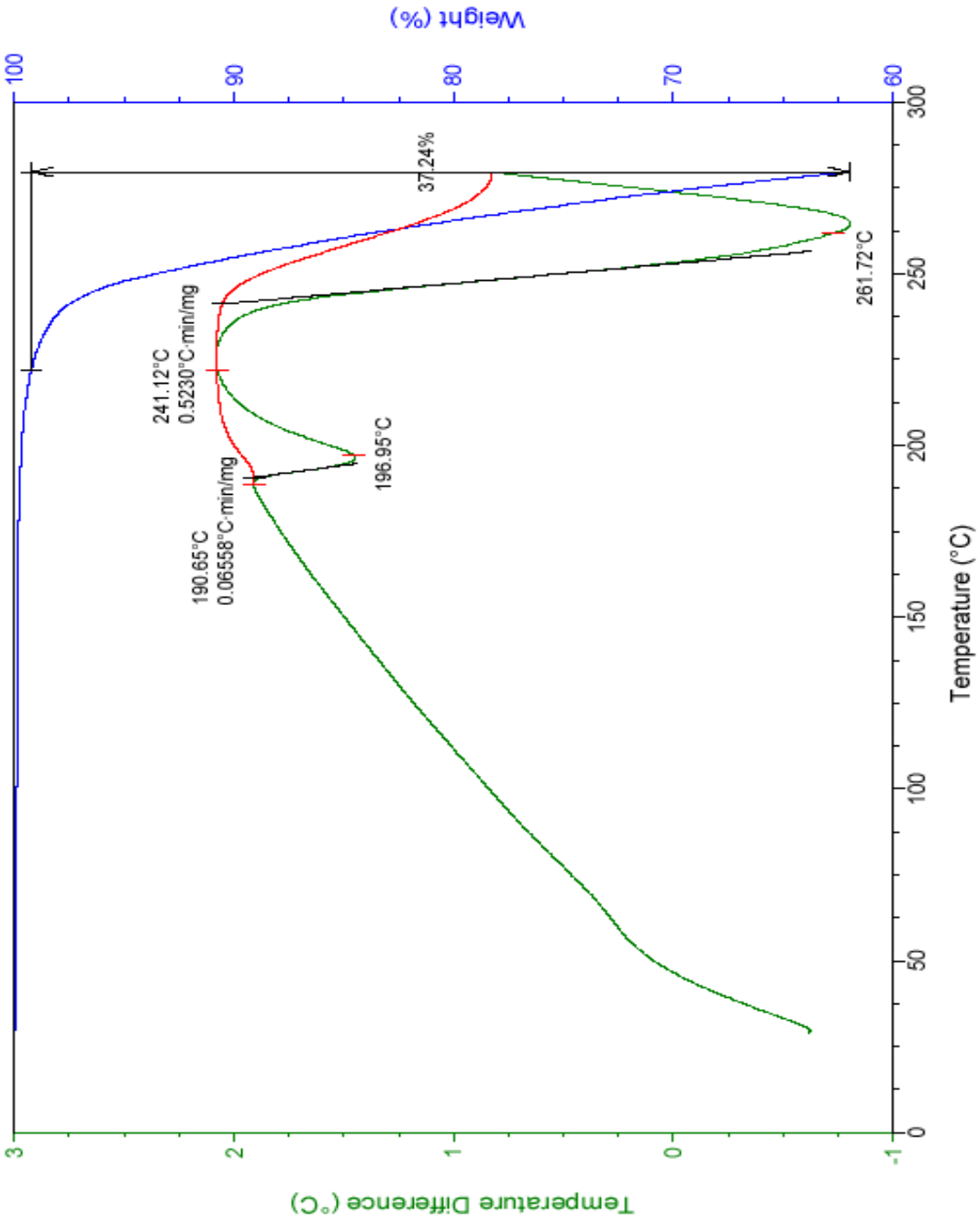

Fig: 3.5 G and DTA Curves of BGM Single crystal

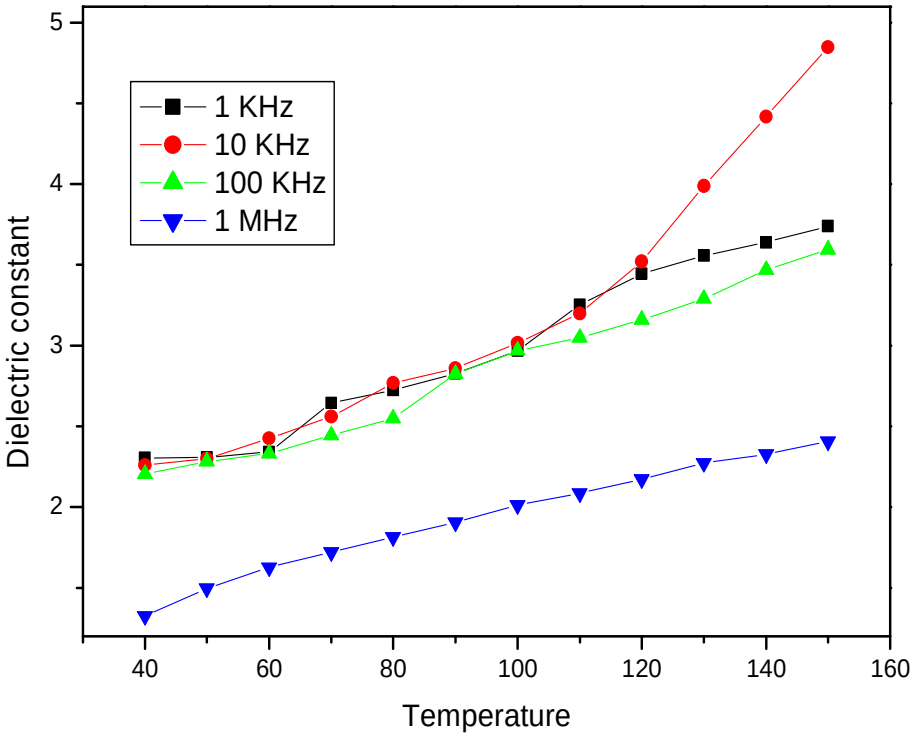

Fig: 3.6 a Variation of dielectric constant as a function of temperature at different frequency

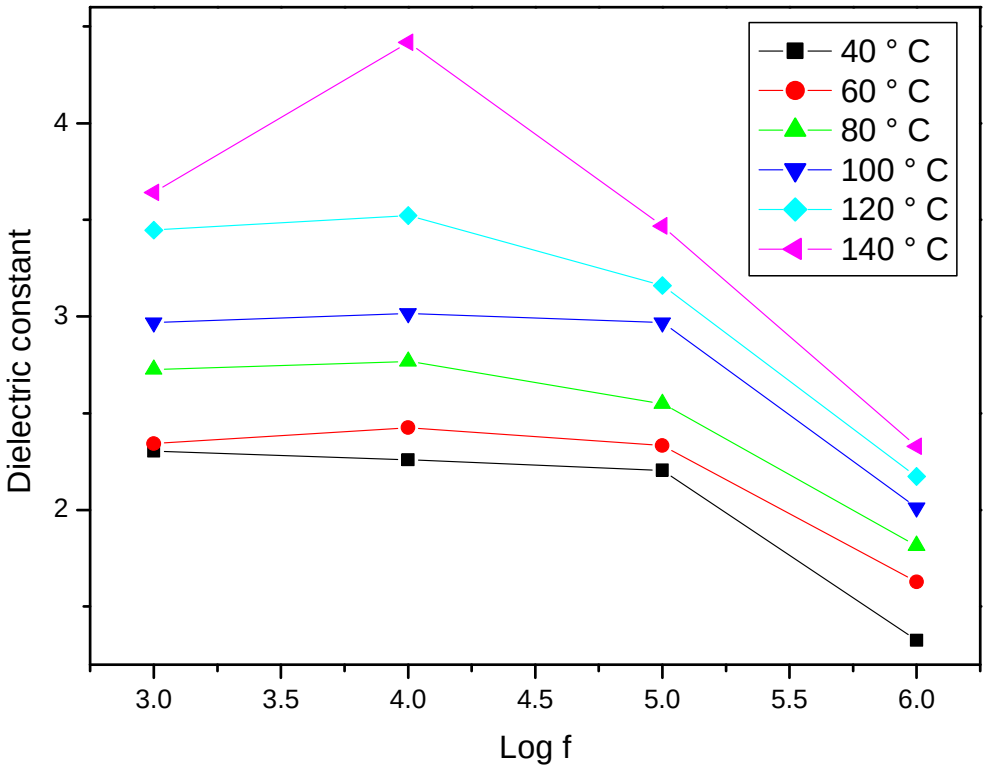

Fig 3.6 b: Variation of dielectric constant as a function of temperature at different frequency

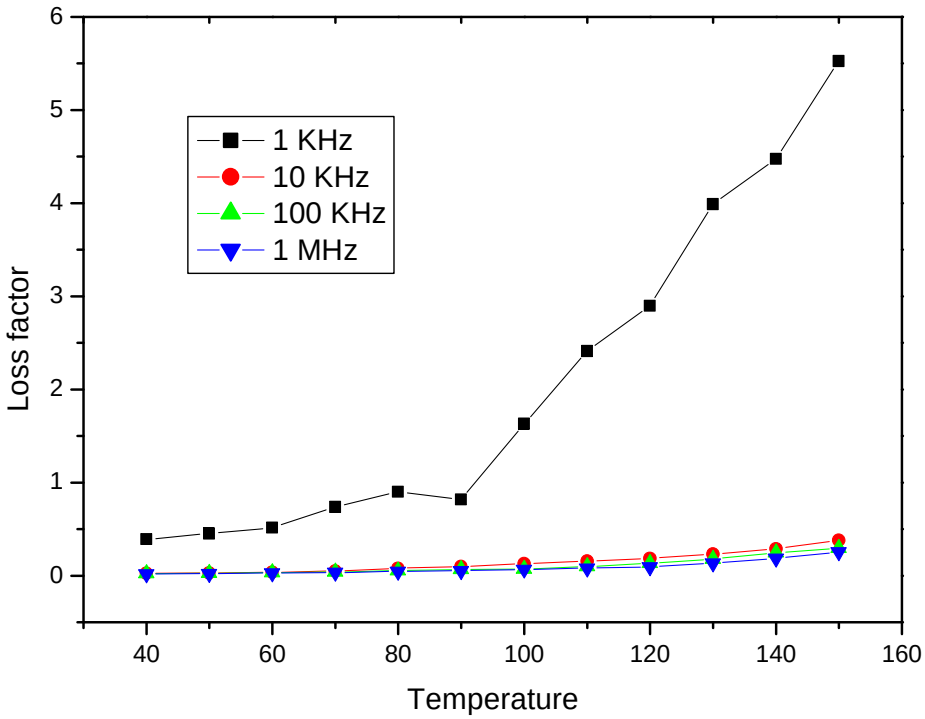

Fig: 3.6 c Variation of dielectric constant as a function of frequency at different temperature

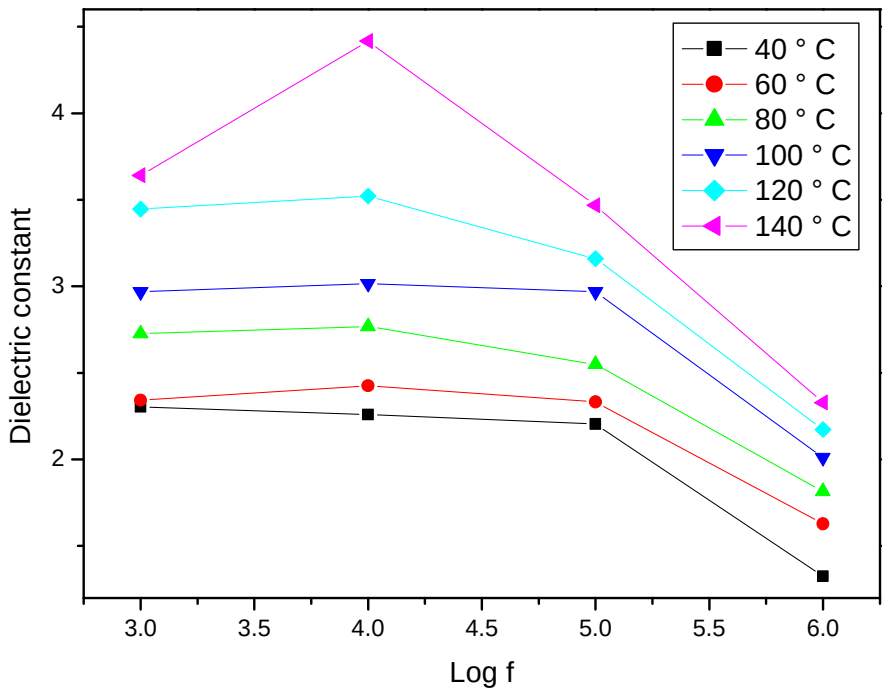

Fig 3.6 d: Variation of dielectric constant as a function of frequency at different temperature

2.1.7 Second harmonic generation

In order to confirm the NLO behaviour in Bis glycine maleate crystal, powdered samples were subjected to Kurtz and Perry powder technique which remains the powerful tool for initial screening of materials for SHG. The second harmonic signal generated in the crystalline sample was confirmed from the emission of green radiation (λ = 534

nm) from the crystal. The measured amplitude of second harmonic green light for Bis glycine maleate is 127.4mV against 54mV for KDP crystal. This result shows a powder SHG efficiency of Bis glycine maleate grown in the presence of 10% mol Ammonium hydroxide was about 1.3 times that of KDP. Due to zwitterion nature γ-glycine crystal has high dipole moment and high melting point which leads to high optical nonlinearity. The main contributions of the higher nonlinear optical properties of γ-glycine are the presence of the hydrogen bond and the vibrational part of the hydrogen bond vibrations. The good second harmonic generation efficiency indicates that the Bis glycine maleate crystals can be used for application in nonlinear optical devices.

CONCLUSION

Bulk single crystals of BGM have been successfully grown by the slow evaporation technique from the aqueous solution. Single crystal X-Ray diffraction method reveals that the structure of grown BGM crystals belongs to hexagonal crystal system. FTIR trace reveals the presence of amino groups and functional groups. The photoconductivity investigations reveal the positive photoconductivity nature of the material. Thermal analysis clearly illustrates that the crystal undergoes decomposition at190.65°C and 241.12°C. Dielectric studies reveal that the sample under investigation possesses good optical quality. The SHG efficiency of the grown crystal was measured by Kurtz powder technique and is 1.3 times that of KDP.

REFERENCES

[1] K.F. Hulme, *Rep. Prog. Phys.* 36 (**1973**) 497.
[2] D.S. Chemla, J. Zyss (Eds.), Nonlinear Optical Properties of Organic Molecules and Crystals, vols. 1 and 2, Academic Press, New York, **1987**.
[3] G. Xing, M. Jiang, Z. Sao, D. Xu, *Chin. J. Lasers* 14 (**1987**) 302.
[4] N. Zhang, M. Jiang, D. Yuan, D. Xu, X. Tao, *Chin. Phys. Lett*. 6 (**1989**) 280
[5] H.O. Marcy, L.F. Warren, M.S. Webb, C.A. Ebbers, S.P. Velsko, G.C. Kennedy, G.L.Catella, *Appl. Opt*. 31 (**1992**) 5051.
[6] Liu X., Z.Wang, G.Zhang, X.Wang, A.Duan, Z.Sun, L.Zhu and D.Xu, **2007**.*J.Cryst.Growth*, 308: 130–132.
[7] Zhang Y., H.Li, B.Xi, Y.Che and J.Zheng, **2008**. *Mater.Chem.Phys*, 108: 192–195.
[8] Hernandez-Paredes., D.Glossman-Mitnik, H.E.Esparza-Ponce M.E.Alvarez-Ramos and A.Duarte-Moller, **2008** *Crystal Journal of Molecular Structure*, 875: 295 –301.
[9] Albrecht G, and R.B.Corey, **1939**. *J.Am.Chem.Soc*, 61: 1087-1103.
[10] Ramachandran E., K.Baskaran and S.Natarajan, **2007**.*Cryst.Res.Technol*, 42: 73–77.
[11] Monaco S B., L.E.Davis, S.P.Velsko, F.T.Wang, D.Eimerl and A.Zalkin, **1987**. *J.Cryst. Growth*, 85: 252-255.
[12] Eimerl D., S.Velsko, L.Davis, F.Wang, G.Loiacona and G.Kennedy, **1989**..*IEEE Quantum Electron*, 25: 179–193.
[13] Aggarwal M., D.Choi, W.S.Wang, K.Bhat, R.B.Lal, Angela D.Shields, G.Benjamin Penn and Donald O.Frazier, **1999**. *J.Cryst.Growth*, 204: 179-183.
[14] Kumaresan P., S.MoorthyBabu and P.M. Anbarasan, **2008**.*Opt.Mater*, 30: 1361-1368.
[15] Yue-zhiCui., Qi Fang, Zhen-li Huang, Gang Xue, Gui-bao Xu and Wen-tao Yu, **2004**.*J.Mater.Chem*, 14: 2443-2447.
[16] Jayanty S., P.Gangopadhyay and T.P.Radhakrishnan, **2002**. *J. Mater.Chem*, 12: 2792-2796.
[17] H.L. Bhat, *Bull. Mater. Sci*.7 (**1994**) 1233.
[18] R. Pepinsky, Y. Okaya, D.P. Eastman, T. Mitsui, *Phys. Rev*. 107 (**1957**) 1538.
[19] R. Pepinsky, K. Vedam, Y. Okaya, *Phys. Rev*. 110 (**1958**) 1309.
[20] Deepthy, H.L. Bhat, *J. Cryst. Growth* 226 (**2001**) 287.
[21] S. Natarajan, J.K. Mohan Rao, Z. *Kristallogr*. 152 (**1984**) 179.
[22] P. Narayanan, S. Venkataraman, Z. *Kristallogr*. 142 (**1975**) 52.
[23] S. Hoshino, T. Mitsui, F. Jona, R. Pepinsky, *Phys. Rev*. 107 (**1957**) 125.
[24] K. Ravikumar, S.S. Rajan, Z. *Kristallogr*. 171 (**1985**) 201.
[25] M. Narayan Bhat, S.M. Dharmaprakash, *J. Cryst. Growth* 235 (**2002**) 511.
[26] T. Balakrishnan, K. Ramamurthi, *Cryst. Res. Technol*. 41 (**2006**) 1184
[27] Weissbuch I., L.Addadi, L.Leiserowitz and M.Lahav, **1998**. *J.Am.Chem.Soc*, 110: 561-564
[28] Narayan Bhat., and S.M.Dharmaprakash, **2002**. *J.Cryst.Growth*, 242: 245 –252.
[29] Ashok Kumar R., R.EzhilVizhi, N.Sivakumar, N.Vijayan and D.RajanBabu, **2012**. *Optik*, 123: 409–413.
[30] Anbuchezhiyan M., S.Ponnusamy, S.P.Singh, P.K.Datta and C.Muthamizhchelvan, **2010**..*Cryst.Res.Technol*, 45: 497 –502.
[31] Dillip G.R., P.Raghavaiah, K.Mallikarjuna, C.Madhukar Reddy, G.Bhagavannarayana, V. Ramesh Kumar and B.Deva Prasad Raju, **2011**. *Crystal Spectrochim.Acta* A, 79: 1123–1127.
[32] Sekar .C, and R. Parimaladevi, **2009** *Spectrochim.Acta A*, 74: 1160 –1164.

[33] Sd.Zuliqar Ali Ahamed.,G.R.Dillip, P.Raghavaiah, K.Mallikarjuna and B.Deva Prasad Raju, **2011**. *Arab.J.Chem*, 5: 234-237.
[34] Parimaladevi R, and C.Sekar,**2010**. *Spectrochim.Acta A*, 76: 490-495.
[35] AnbuchudarAzhagan S, and S.Ganesan, **2012**. *Optik*, 3: 13-17.
[36] Narayana Moolya B., A.Jayarama, M.R.Sureshkumar and S.M.Dharmaprakash, **2005**. *J.Crystal Growth*, 280: 581 –586.
[37] Baraniraj T, and P.Philominathan, **2011**. *J.Miner.Mater.CharactEng*, 10: 351-356.
[38] Surekha R., R.Gunaseelan, S.Selvakumar, P.Sagayaraj and K.Ambujam, **2011**.*Arch.Appl.Sci.Res*, 3: 280–295.
[39] Dhanraj P .V, and N. P. Rajesh, **2011**. *Mater.Chem.Phys*, 115: 413–417.
[40] Balasubramanian D., P.Murugakoothan and R.Jayavel, **2010**. *J.Crystal Growth*, 312: 1855 –1859.
[41] Ambujam K., S.Selvakumar, D.PremAnand, G.Mohammad and P.Sagayaraj, **2006**. *Cryst.Res.Techno*, 41: 671 – 677.
[42] Mott B.W., **1956**. Micro indentation Hardness Testing, Butterworth, London.
[43] Sun Z. H., W.T.Yu, X.F.Cheng, X.Q.Wang, G.H.Zhang, G.Yu, H.L.Fan and D.Xu, **2008**..*Opt.Mater*, 30:1001-1004.
[44] Milton Boaz B., Babu Varghese, C.Justin Raj and S.Jerome Das, **2007**. *Materials Science and Engineering* B, 136: 57–61.