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Synthesis, Growth and characterization of Bis - glycine cobalt chloride dihydrate single crystal: A new semiorganic nonlinear optical material

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Abstract:

Single crystals of potential semiorganic nonlinear optical material of bis - glycine cobalt chloride dihydrate (BGCC) were grown by slow evaporation technique at room temperature. The structure of BGCC crystal was examined by single crystal X – ray diffraction analysis. The single crystal X – ray diffraction of BGCC reveals that the crystal belongs to monoclinic system with centrosymmetric space group. The powder X – ray diffraction analysis was carried out the reflection planes of the sample was confirmed and the peaks were indexed. Fourier transform infrared (FT – IR) spectroscopic analysis was used to confirm the presence of various functional groups in the grown crystal. UV – Vis – NIR spectral analysis of BGCC crystal shows that the crystal is transparent between the wavelengths 265 nm to 1100 nm. Vickers microhardness study revealed that the grown crystal belongs to soft material category. Dielectric constant and dielectric loss of BGCC crystal were measured in the frequency range of 100 Hz to 3 MHz. Thermal stability of the BGCC crystal was studied by thermogravimetric, differential thermal analysis and differential scanning calorimetric studies and found that the grown crystal is stable up to 220 °C.

1. Introduction

Nonlinear optical (NLO) materials have been playing an increasingly important role in laser science and technology. Among NLO materials, organic NLO materials are generally believed to be more versatile than their inorganic counterparts due to their more favorable nonlinear response. In the organic class, α – amino acids exhibit some specific features [1] such as molecular chirality, weak van der Walls and hydrogen bonds and the absence of strongly conjugated bonds, wide transparency ranges in the visible and UV spectral region and zwitterionic nature of the molecule which favors crystal hardness [2]. Other advantages of organic compounds apart from the above include amenability for synthesis, multifunctional substitutions, higher resistance to optical damage and maneuverability for device applications, etc. Amino acids contain both a carboxyl group (COOH) and an amino group (NH_2). Glycine is the smallest amino acid and for this reason it fits into crowded regions of many peptide chains, being used in the synthesis of many protein and non – protein compounds. It is the only α – amino acid that is not optically active [3]. The amino acid, glycine has three crystal forms, α, β and γ [4] polymorphs, α and γ remain unchanged for a long time under normal conditions [5] and β polymorph is unstable, whereas α is known to transform to the γ form. All of the other amino acids contain an asymmetric or “chiral” carbon atom and are, therefore, optically active [6]. Glycine form complexes with mineral acids exhibiting interesting physical properties like ferroelastic, ferroelectric or anti - ferroelectric behavior [7]. BGHC [8, 9], Glycine$_2$ Zncl$_2$.$2H_2O$, Glycine$_2$ CaI$_2$.$3H_2O$ [9] and BGHB [10, 11] are some of the grown and already reported bis glycine single crystals. In the present work, we have attempted to grow single crystals of bis - glycine cobalt chloride (BGCC) by slow evaporation technique at room temperature. The bis – glycine cobalt chloride dihydrate single crystal structure was reported by Stenzel and Michel Fleck [12]. A thorough scan on literature reveals that no systematic work has been done to grow BGCC as single crystal. The grown crystal of BGCC have been investigated and discussed. We are reporting spectral, optical, thermal, dielectric and hardness properties of grown BGCC crystals for the first time to the best of our knowledge and belief.

2. Experimental procedure

2.1 Synthesis

Synthesized BGCC salt was produced by dissolving glycine and cobalt chloride hexahydrate in double distilled water in the stoichiometric ratio 2:1 at room temperature. The solution was stirred well for 4 h using temperature controlled magnetic stirrer to obtain a homogeneous mixture. Then the solution was allowed for evaporation at room temperature and then synthesized salt was obtained. The chemical reaction is follows

$$2(CH_2NH_2COOH)+CoCl_2.6H_2O\rightarrow Co[(CH_2NH_2COOH)_2.2H_2O].Cl_2$$

2.2 Crystal growth

Single crystals of BGCC were successfully grown by slow evaporation technique at room temperature. The saturated solution of BGCC was prepared using the synthesized salt and the solution was thoroughly stirred to avoid the co precipitation of the salt. To improve the purity of the synthesized salt by recrystallization process and the process was repeated more than twice. The prepared saturated solution was filtered using Whatman filter paper. The beaker containing the solution was tightly closed with perforated polythene sheet and placed in an undisturbed atmosphere for controlled evaporation. Single crystals of size 5 × 5 × 3 mm^3 were harvested in a growth period of two weeks. As grown single crystals of BGCC is shown in Fig.1.

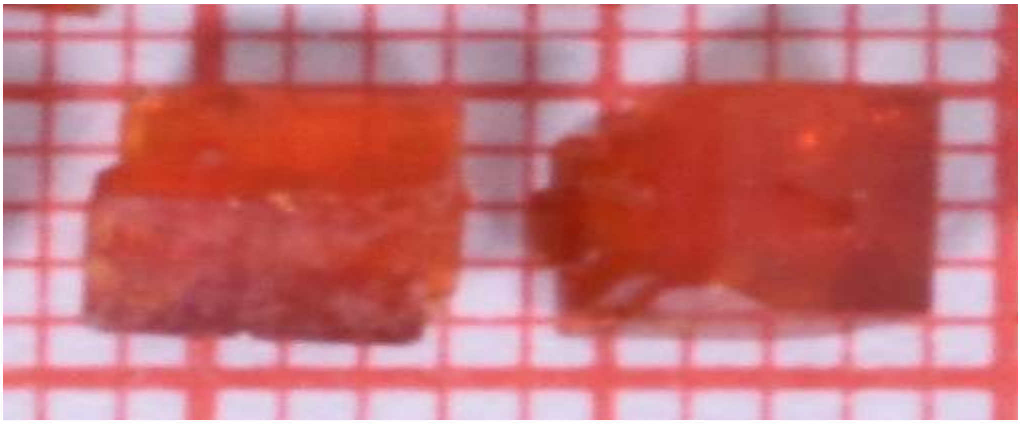

Fig. 1 As grown single crystal of BGCC

3. Result and discussion

3.1 Single crystal X- ray diffraction analysis

Single crystal X – ray diffraction analysis for the grown BGCC crystals were carried out to confirm the crystallinity and identification of the unit cell parameters using ENRAF NONIUS CAD – 4 X – ray diffractometer. The grown BGCC crystal was subjected to single crystal X – ray diffraction study to obtain the crystallographic data which revealed that BGCC crystal belongs to centrosymmetric space group with monoclinic system. Single crystal X – ray diffraction data for BGCC is presented in Table 1. The determined single crystal XRD data and structure refinement of BGCC are in good agreement with the reported ones [12].

3.2 Powder X – ray diffraction analysis

Powder X – ray diffraction study was carried out employing SEIFERT JSO DEBYEFLEX (Model 2002) diffractometer with Cu Kα (1.5405Å) radiation. The grown BGCC crystal was crushed to a uniform fine powder and subjected to powder X – ray diffraction to identify the reflection planes. The powdered sample was scanned over the 2θ range of 10 - 80° at a rate of 1°/ min. The well – defined peaks at specific 2θ values show high crystallinity of the grown crystal. From the X – ray diffraction data the various planes of reflections were indexed using the software AUTOX 93. The indexed powder X - ray diffraction pattern of the grown BGCC is given in Fig. 2.

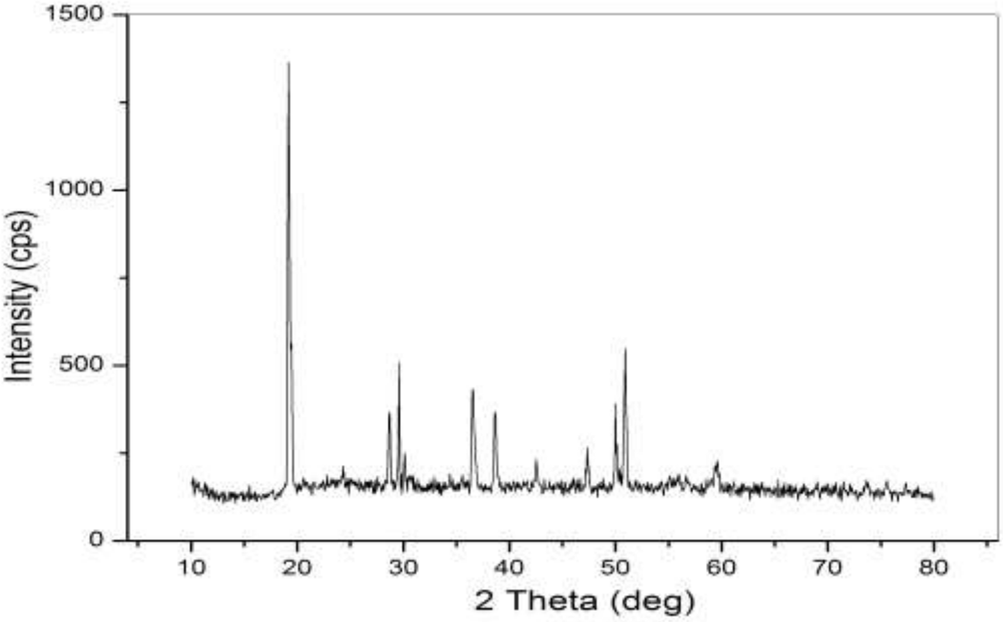

Fig. 2 Powder X – ray diffraction of BGCC

Table 1 Crystal data for BGCC single crystal

Molecular Formula	$Co[(C_2H_5NO_2)_2.2H_2O].Cl_2$
Formula weight	314
Temperature	294 (2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a= 10.464 (2) Å α = 90°
	b= 5. 766 (2) Å β = 91.57 (2)°
	c= 8.758 (4) Å γ = 90°
Volume	560. 54 (3) Å^3

3.3 FT – IR spectral analysis

Fourier transform infrared (FT – IR) spectrum was recorded by Perkin Elmer FT – IR spectrometer using KBr pellet technique in the range 400 – 4000 cm^{-1}. The FT – IR spectrum of BGCC is shown in Fig. 3. The N – H stretching vibrational bands are observed at 3382 and 3277 cm^{-1} respectively. The C – H symmetric stretching vibration is observed at 3180 cm^{-1}. The very strong peak observed at 1611 cm^{-1} is assigned to asymmetric stretching vibration of the COO$^-$. The band at 1090 cm^{-1} is assigned to the C – C – N asymmetric stretching vibration. The strong band appearing at 711 cm^{-1} in the spectrum is assigned to N – C - Co ring deformation. Metal – glycine coordination through the nitrogen (N) and one carboxylate oxygen (O), forming a five member ring, is commonly found in these compounds. It is established that the Co – OH stretching vibration of cobalt (604 cm^{-1}) is shifted to a lower wave number of BGCC (590 cm^{-1}). The Co – N + Co – O (or) O – Co – N stretching vibration of cobalt (495 cm^{-1}) is shifted to a higher wave number of BGCC (502 cm^{-1}) and Co - N stretching vibration of cobalt (422 cm^{-1}) is shifted to a lower wave number of BGCC (417 cm^{-1}), which clearly indicates the coordination of nitrogen with metal atom. The observed bands along with their vibrational assignment are summarized and presented in Table 2.

Table 2 Tentative vibrational band assignments of BGCC single crystal

Present work	Reported [3]	Band assignments
3460	3429	O – H stretching vibration
3382	3286	N – H stretching vibration
3277	3258	N – H stretching vibration
3180	3160	C – H stretching vibration
1611	1605	COO$^-$ asymmetric stretching vibration
1481	1466	NH_3 deformation
1388	1374	CH_2 symmetric stretching vibration
1090	1071	C – C – N asymmetric stretching vibration
711	720	N – C – Co ring deformation
590	604	Co – OH vibration
502	495	(CoN – CoO) or (O – Co – N) vibration
417	422	Co – N stretching vibration

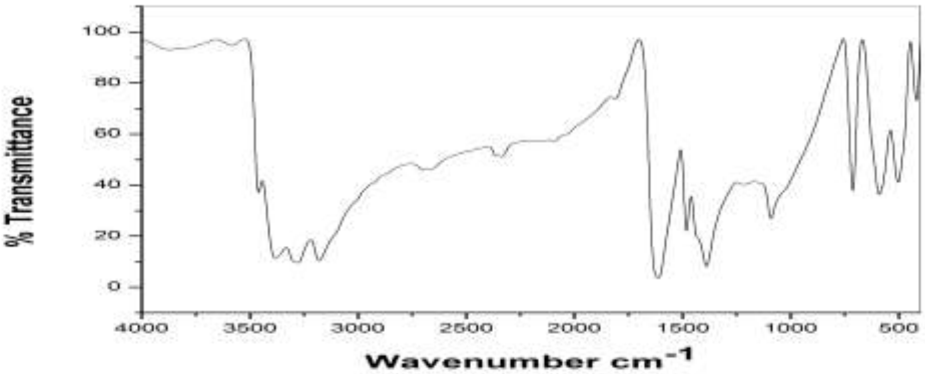

Fig. 3 FT – IR spectrum of BGCC single crystal

3.4 Optical transmission studies

The optical transmission spectrum was recorded in the range 190 – 1100 nm using Varian Cary 5E spectrophotometer. Figure 4 shows the optical absorption spectrum of a BGCC single crystal. From the spectrum, it is evident that the BGCC crystal has a very low lower cutoff wavelength of 265 nm, along with a large transmission window in the entire region. Hence, it can be utilized for SHG from a laser operating at 1064 nm or other optical applications in the blue region. The UV cutoff wavelength of the BGCC (265 nm) is thus comparable to other bis glycine complexes of NLO crystals such as BGHC (around 300 nm) [7] and BGHB (below 300 nm) [10].

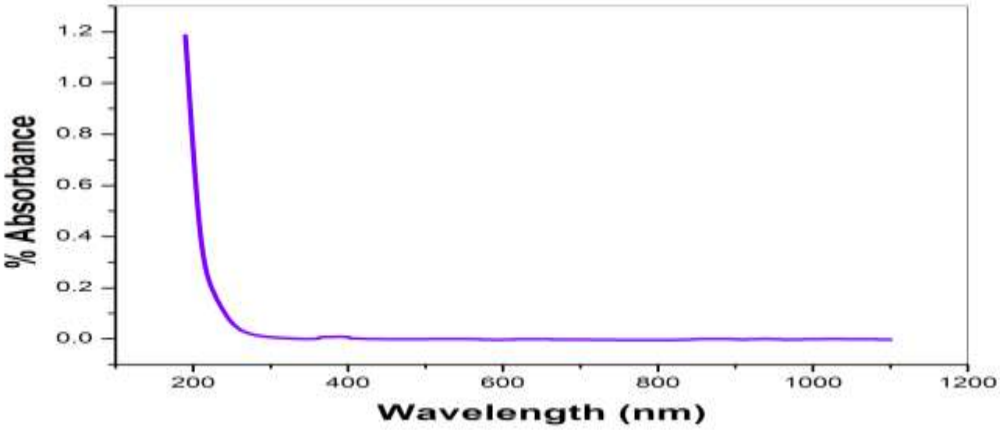

Fig. 4 Optical absorption spectrum of BGCC single crystal

3.5 Microhardness Studies

Micro hardness studies of any system has a direct correlation with the crystal structure and are very sensitive to the presence of any other phase or phase transition and lattice perfections prevalent in the system. The hardness of the material depends on the different parameters such as lattice energy, Debye temperature, heat of formation and interatomic spacing. The Vickers microhardness analysis was carried out by Vickers microhardness tester fitted with a diamond indentor. A well polished BGCC crystal of 2 mm thickness was placed on the platform on the Vickers microhardness tester and loads of different magnitude was applied over a fixed interval of time. The indentation time was kept as 10s for all trials.

The Vickers microhardness number was evaluated from the relation $H_v = 1.8455\ (P/\ d^2)$ kg/ mm^2 [13], where H_v is the Vickers hardness number, P is the applied load in kg. d is the diagonal length of the impression in mm and 1.8455 is a constant, that is a geometrical factor for the diamond pyramid. Figure 5 shows the variation of Vickers hardness number (H_v) with applied load (P) of the BGCC single crystal. At each load two indentations were made and the mean diagonal length of indentation was used. It is seen from the graph that the hardness value of the grown crystal increases with an increase of load. For an indentation load of 100g, cracks were developed on the crystal surface, around the indenter. Both linear cracks along the diagonal of the impression and curved cracks along the edges of indentations were observed.

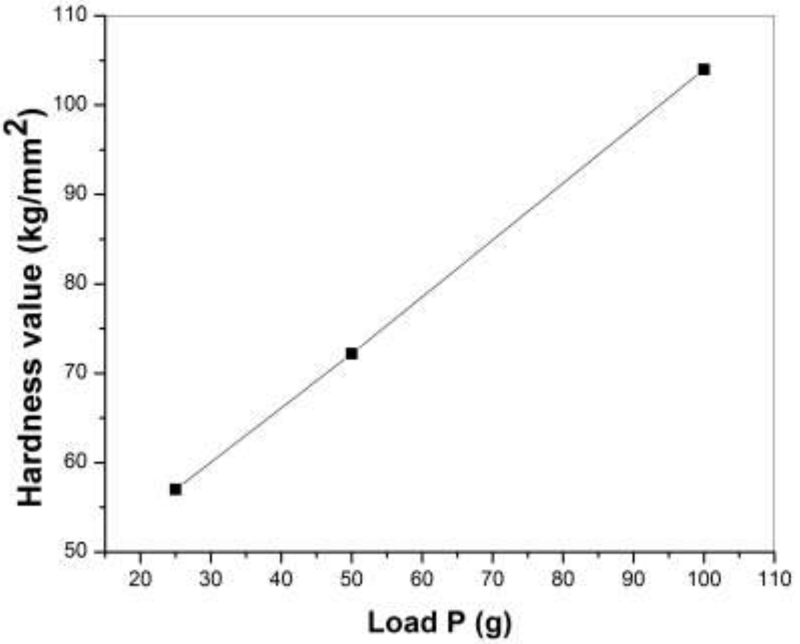

Fig. 5 Variation of Vickers hardness number (Hv) Vs Load P for BGCC

The microhardness measurements were limited to 100 g of load because the crack formation was high beyond 100 g. This is due to the release of internal stress locally initiated by indentation. The relation between load and size of the indentation is given by well known Meyers power law $P = Ad^n$. Here A and n are constants depending upon the material [14]. The work hardening coefficient value (n) of the grown crystal was determined from Fig. 6 by the least squares curve fitting method. The n value of BGCC was found to be 3. According to Onitsch and Hanneman, n should lie between 1 and 1.6 for hard materials and above 1.6 for softer ones [15, 16]. Hence, it is concluded that BGCC crystal is under soft material category.

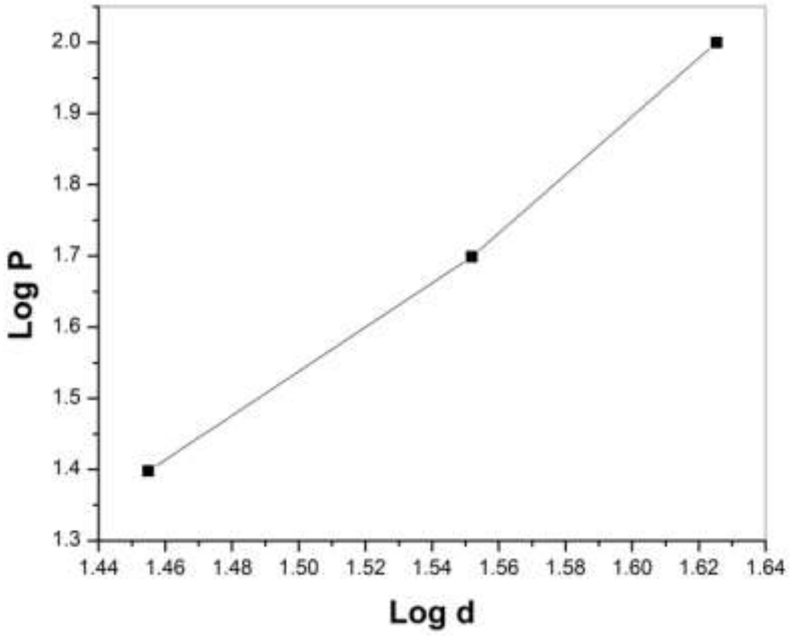

Fig. 6 Plot of log P Vs log d of BGCC single crystal.

3.6 Dielectric studies

The dielectric property of the BGCC single crystal was measured using an HIOKI LCR HIGHTESTER meter. Typical sample dimensions were 3 × 3 mm^2 in surface area and 2 mm thickness of the crystal was used for this study. The opposite faces of the samples were painted using silver paste. A two terminal copper electrode was used as sample holder and the sample was held between the electrodes. A thermo couple was fixed in the vicinity of the lower electrode to measure the temperature of the sample. In this way a parallel plate capacitor was formed. The capacitance of the sample was measured by varying the frequency from 50 Hz to 3 MHz. Dielectric constant of the material was calculated using the relation $\varepsilon_r = Cd/(\varepsilon_0 A)$, where A is the area of the plate, d is the distance between the two parallel plates. ε_0 is the absolute permittivity of the free space. Figure 7 and 8 shows the variation of dielectric constant and dielectric loss are maximum for lower frequency and minimum for higher frequencies, which is due to the space charge polarization [17].

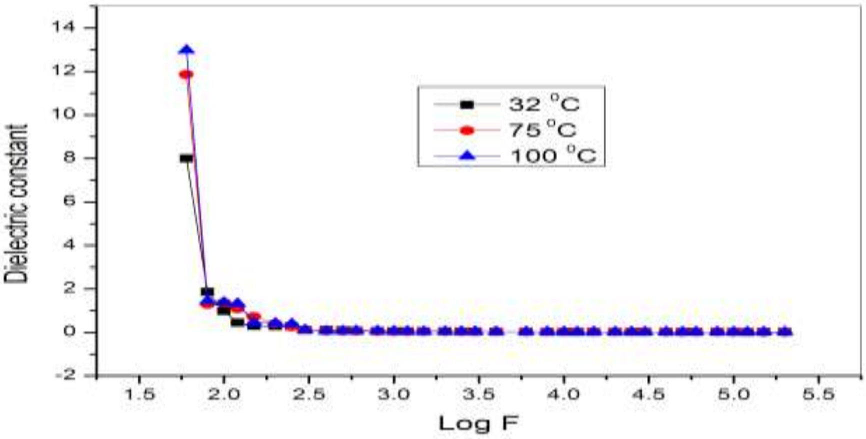

Fig. 7 Dielectric constant of BGCC single crystal

A high value of dielectric constant at low frequency region indicates that there is contribution from all four known sources of polarization that are electric, ionic, dipolar and space charge polarization. The presence of bound water molecules weakens the dielectric constant while the frequency increased. While temperature is increased the bound water molecules get activated resulting in high dielectric constant. Since water has high dielectric constant, the activation of bound water at higher temperature may be responsible for increase of dielectric constant. The characteristics of low dielectric constant and dielectric loss with high frequency for a grown crystal indicate the presence of lesser defects and this parameter is of most important for various nonlinear optical applications [18].

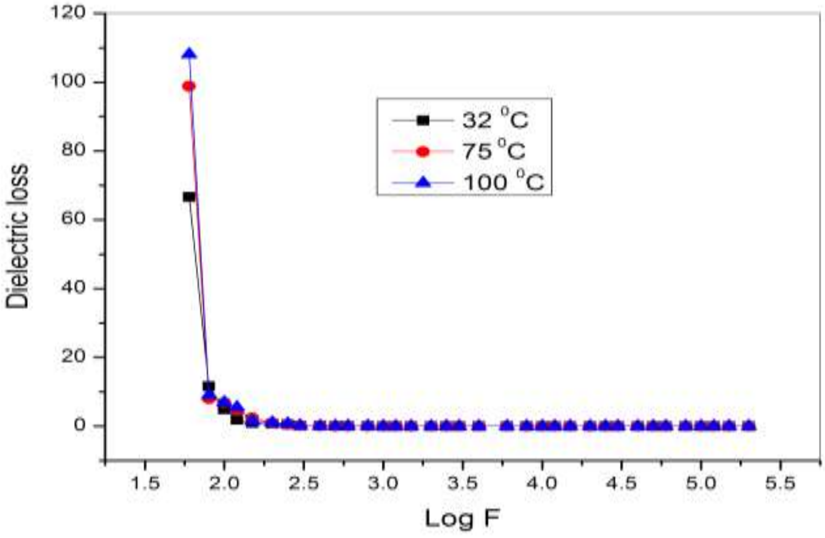

Fig. 8 Dielectric loss of BGCC single crystal

3.7 Thermal analysis

Thermogrametric analysis (TGA) and Differential Thermal Analysis (DTA) are very important characteristic techniques to identify the thermal stability of the material for fabrication where a considerable amount of heat is generated during the cutting process. Thermal analysis was carried out on the grown crystals to study the thermal stability and melting point. TGA and DTA curves were recorded for the BGCC crystal using SDT Q600 V8.3 Build 101 thermal analyzer in the range of temperature from 25° to 1000 °C at a heating rate of 20°C / min in nitrogen atmosphere with a ceramic crucible for heating the sample. The initial mass of the material subjected to analysis was 3.5840 mg. The TGA and DTA thermogram of the grown crystal is shown in Fig. 9. For BGCC, the TGA trace appears nearly straight up to 220 °C. It is observed that the BGCC decomposes into two stages. The first stage of decomposition occurs at 223 °C to 282 °C, which is due to the removal of two water molecules and two glycine molecules. Second stage of decomposition starts at 282 °C to 639 °C and it is due to the removal of remaining cobalt chloride molecule.

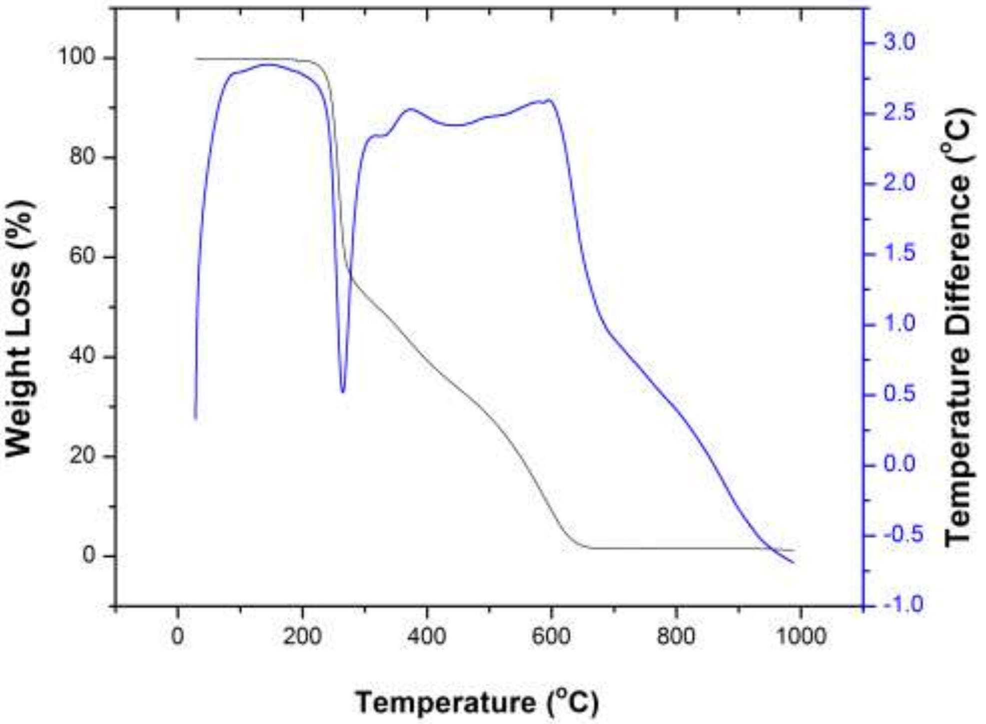

Fig. 9 TGA/DTA plot of grown BGCC single crystal

4. Conclusion

Optically good quality single crystals of BGCC were conveniently grown by slow solvent evaporation method. The crystallinity of the grown crystals was confirmed by powder X – ray diffraction studies. The single crystal X – ray diffraction analysis confirmed BGCC crystal belongs to monoclinic crystal structure. FT – IR studies show that in the spectrum of BGCC there is a shift in the frequency band in the low frequency region which reveals that glycine forms chloride – to – cobalt in the BGCC crystal. Optical transmittance studies shows that the grown crystal was optically transparent even up to near IR region and the lower cut of wavelength occurs around at 265 nm. Vickers microhardness value was calculated in order to understand the mechanical stability of the grown crystals. The reverse indentation size effect for grown crystal was conformed from mechanical studies. The dielectric constant and dielectric loss of the grown BGCC crystal decreases with increase in frequency and these low values at high frequencies reveal the desirable property of the crystal for NLO applications. TGA and DTA thermograms reveal that the grown crystal is thermally stable up to 220 °C.

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