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SPECTRAL AND DIELECTRIC PROPERTIES OF TRIGLYCINE BARIUM DICHLORIDE DIHYDRATE NLO SINGLE CRYSTAL

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Abstract. Single crystals of Triglycine barium dichloride dihydrate were grown by slow evaporation technique. The unit cell dimensions and space group of the grown crystals were confirmed by single crystal X-ray diffraction. The functional groups present in the structure of the grown crystal are identified by using FTIR spectral analysis. The microhardness study shows that the Vickers hardness number of the crystal increases with the increase in applied load. Dielectric constant and dielectric loss measurements were carried out for different temperatures and frequencies.

1. Introduction

In the modern world, the development of science in many areas has been achieved through the growth of single crystals. Large sized single crystals are essential for device fabrication and efforts are taken to grow large single crystals in short duration with less cost. Over the past two decades much attention has been paid to the search of novel high quality NLO materials that can generate high second order optical nonlinearities which IS important for potential applications including telecommunication, optical computing, and optical data storage and processing [1-6]. The present investigation deals with the growth of Triglycine barium dichloride dihydrate single crystal by slow solvent evaporation technique and the characterization of the grown crystal. The grown crystals were characterized by single crystal and powder X-ray analysis, FTIR and UV spectral analysis, microhardness, dielectric, and SHG measurements. The results of these studies have been discussed.

2. Experimental procedure

Triglycine barium dichloride dihydrate crystal was synthesized by dissolving glycine and barium dichloride dihydrate in the stoichiometric ratio (3:1) in double distilled water. The synthesized salt was purified by successive recrystallization process. Supersaturated solution of Triglycine barium dichloride dihydrate was prepared and filtered. The filtered solution was kept in a beaker covered with porous papers and kept in a dust-free atmosphere. After a period of 24 days, colorless and transparent crystals were obtained.

3. Characterizations

The characterization studies includes single XRD and powder XRD analysis, UV and FTIR spectral analyses, mechanical and dielectric studies of the grown crystals. The grown crystal

Triglycine Barium Dichloride Dihydrate in the present investigations is exhibiting NLO property more than that of KDP, these grown materials can be used as a better replacement for KDP to find applications in the field of opto-electronics. Hence, the grown crystals are to be confirmed for the single crystalline nature using XRD technique. The grown crystals are characterized by UV and FTIR analyses to analyze the transmission range of the incident light and the presence of functional groups present in the material. From UV spectral analysis the required transmission range for the Second Harmonic Generation (SHG). UV spectral analysis reveals the large transparency nature of the grown materials. The mechanical, dielectric studies were carried out to probe the mechanical strength and polarizability nature of the grown crystals for the suitability of the materials under various conditions to find the applications in various fields.

3.1. Single crystal XRD. The single crystal X-ray diffraction has been carried out using Enraf Nonius-CAD4 diffractometer. The data obtained show that the grown specimen of Triglycine barium dichloride dihydrate crystal belongs to orthorhombic system with lattice parameters a = 8.27 Å, b= 9.28 Å, c = 14.83 Å, $\alpha = \beta = \gamma = 90^\circ$. XRD results are in good agreement with the already reported values [7].

3.2. Powder X-ray diffraction analysis. X-ray powder diffraction was used to confirm single crystal XRD results. Efforts were made to record the powder XRD pattern of the Triglycine barium dichloride dihydrate crystal and index them. The indexed powder XRD pattern of the grown Triglycine barium dichloride dihydrate crystal is shown in Fig.1. The appearance of sharp and strong peaks confirms good crystallinity of the grown sample. From the data, the lattice parameters were calculated as a = 8.27 Å, b= 9.28 Å, c = 14.83 Å, $\alpha = \beta = \gamma = 90^\circ$. The results agree well with single crystal XRD results and the available literature values [7].

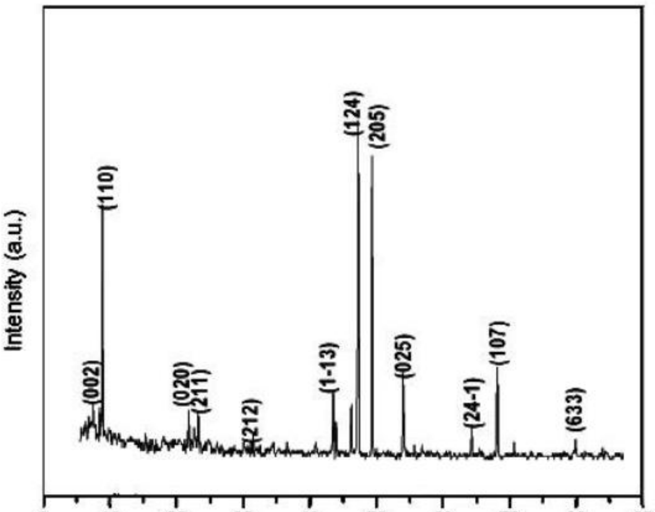

Fig. 1. Powder X-ray diffraction pattern.

3.3. FTIR analysis. The FTIR spectrum for Bisglycine hydrobromide was recorded in the region 4000 cm^{-1} – 500 cm^{-1} employing BRUKER IFS 66V spectrometer and FTIR spectrum as shown in Fig. 2. The sharp peak at 3429, 3480 and 2992 cm^{-1} may be assigned to NH_3^+ stretching band. The asymmetric stretching vibration of CH_2 group appears at 2585 cm^{-1}. The asymmetric and symmetric stretching modes of COO^- groups are confirmed by the peaks at 1497, 1446, 1335, and 1254 cm^{-1}. The absorption bands occurred at 1029 and 896 cm-1 due to C- C- N and C- C stretching modes respectively. The presence of NH_3^+ and

COO^- group showed the zwitter ionic nature of the glycine molecule in Triglycine barium dichloride dihydrate crystal. FTIR spectral analysis thus identifies the presence of functional group in the grown material Triglycine barium dichloride dihydrate.

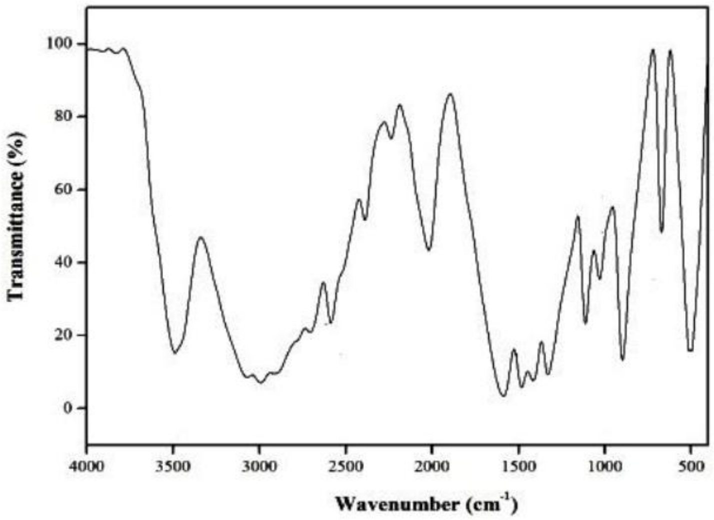

Fig. 2. FTIR spectrum of Triglycine barium dichloride dihydrate single crystal.

3.4. UV-visible spectral analysis. To determine the transmission range and hence to know the suitability of Triglycine barium dichloride dihydrate single crystals for optical applications, the UV–vis spectrum was recorded in the range of 200–1000 nm as shown in Fig. 3. The lower cut off of the Triglycine barium dichloride dihydrate crystal is at 310 nm and the range of transparency in UV and visible region makes it a very potential material for blue light emission. Hence, the material can be used for second harmonic generation (SHG) applications, using the powerful light source of wavelength below 600 nm.

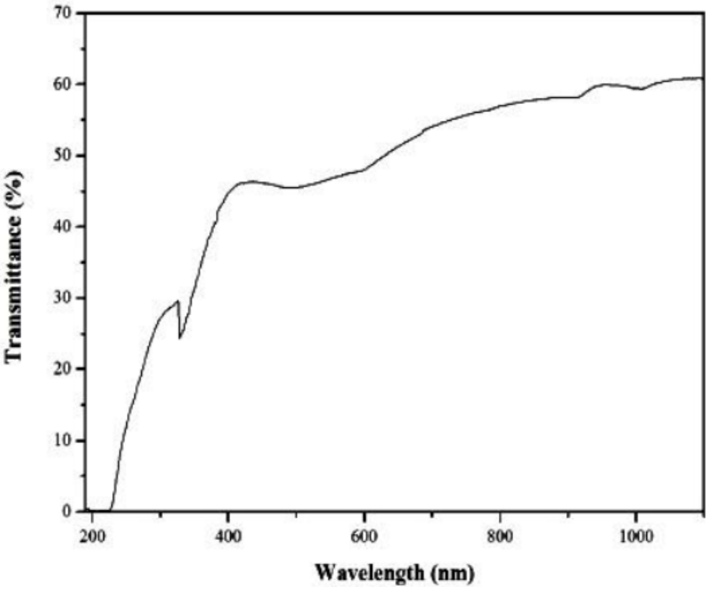

Fig. 3. UV-vis transmittance spectrum.

3.5. NLO studies. The SHG conversion efficiency of Triglycine barium dichloride dihydrate was determined by the modified version of the powder technique developed by Kurtz and Perry. The crystal was ground into powder and densely packed in a micro capillary tube of uniform bore. A Q-switched Nd: YAG laser beam of wavelength 1064 nm with an input power of 6.2 mJ/pulse, and a pulse width of 8 ns with a repetition rate of 10 Hz was made to fall normally on the sample. The output from the sample was monochromated to collect the intensity of 532 nm component and to eliminate the fundamental wavelength. Second harmonic radiation generated by the randomly oriented micro crystals was focused by a lens and detected and a photo multiplier tube. The generation of the second harmonic was confirmed by a strong bright green emission emerging from the powdered sample. A potassium dihydrogen phosphate crystal was used as a reference material in the SHG measurement. The relative conversion efficiency was calculated from the output power of Triglycine barium dichloride dihydrate crystals with reference to KDP crystals. It is observed that the conversion efficiency of Triglycine barium dichloride dihydrate is equal to that of KDP crystals.

3.6. Microhardness property. The microhardness measurements were carried out with a load range from 10 to 50 g. The Vickers microhardness number was calculated using the relation,

$$H_v = (1.8544\, P/d^2), \tag{1}$$

where P is the indenter load and d is the diagonal length of the impression. Figure 4 shows the variation of P with Vickers hardness number (H_v) for grown single crystal. It is evident from the plot that the Vickers microhardness number increases with increasing applied load. According to Meyer’s law, the relation connecting the applied load is given by

$$P = k_1 d^n, \tag{2}$$

where n is the Meyer index or work hardening exponent and k_1, is the constant for a given material. By plotting log P against log d, (Fig. 5) the values of work hardening coefficient was calculated as 2.34 which is greater than 2, establishing that the hardness increases with increase of the load. Large value of n indicates large effect of dislocations.

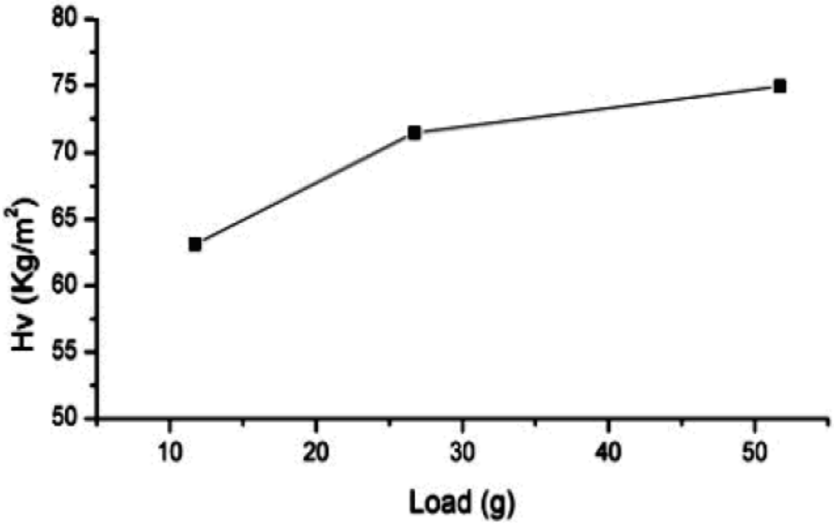

Fig. 4. Variation of *H*v with load *P*.

3.7. Dielectric study. The dielectric study of the grown crystal was carried out using the instrument, HIOCKI 3532-50 LCR HITESTER. A sample of having silver coating on the opposite faces was placed between the two copper electrodes and a parallel plate capacitor was thus formed. The capacitance of the sample was measured by varying the frequency from 100 Hz to 5 MHz and the dielectric constant (ε) Vs applied frequency is plotted (Fig. 6). The dielectric loss is also studied as a function of frequency at different temperatures (Fig. 7). It is observed that the dielectric constant, dielectric loss values are found to decrease with the increase in frequency at all temperatures. The high value of dielectric constant at low frequency may be due to presence of all polarizations and its low value at higher frequencies may be due to the significant loss of all polarizations gradually [8].

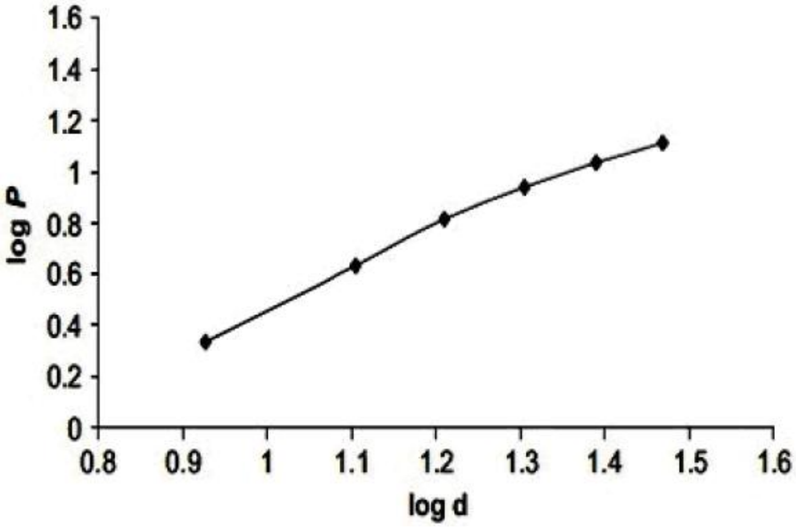

Fig. 5. Plot of log d versus log p.

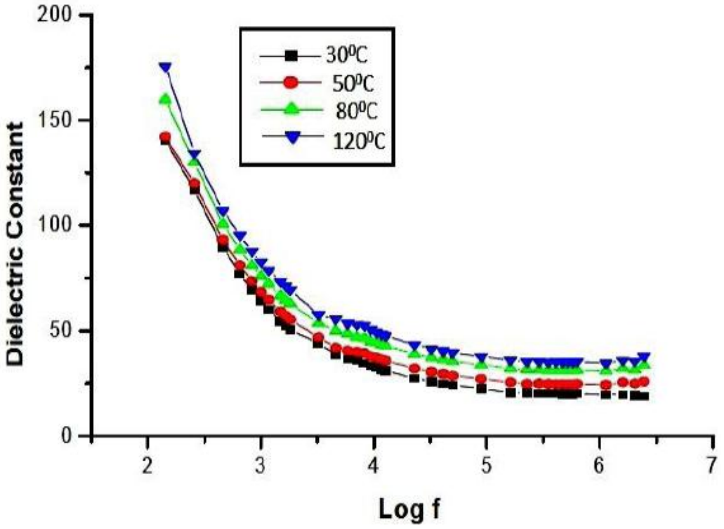

Fig. 6. Dielectric constant vs Log f.

In accordance with Miller rule, the lower value of dielectric constant is a suitable parameter for the enhancement of SHG efficiency. The variation of dielectric constant with temperature is generally attributed to the crystal expansion, the electronic and ionic polarizations and the presence of impurities and crystal defects [9]. The observed lower values of dielectric loss at higher frequencies for this sample suggest that the grown crystal contains less number of defects with high optical quality [10].

4. Conclusions

Single crystals of Triglycine barium dichloride dihydrate were grown by slow evaporation technique. The unit cell dimensions of the grown crystals were confirmed by single crystal X-ray diffraction. Functional groups present in the material have been confirmed by FTIR analysis. UV-visible transmission spectrum shows excellent transmission in the entire visible region. NLO study reveals that the grown crystal has SHG efficiency equal to that of KDP crystal. Mechanical studies were carried out for the grown crystal. Dielectric constant and dielectric loss measurements were carried out at different temperatures and frequencies. The material exhibits NLO behaviour remarkably due to its better optical and dielectric properties.

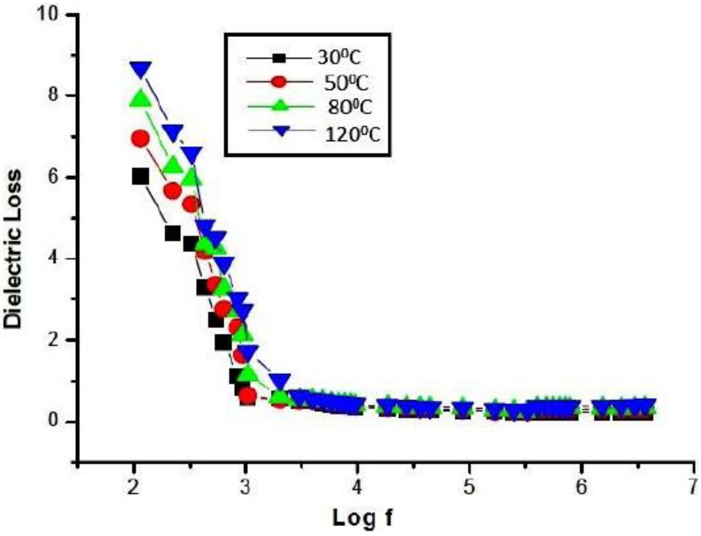

Fig. 7. Dielectric loss vs Log f.

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