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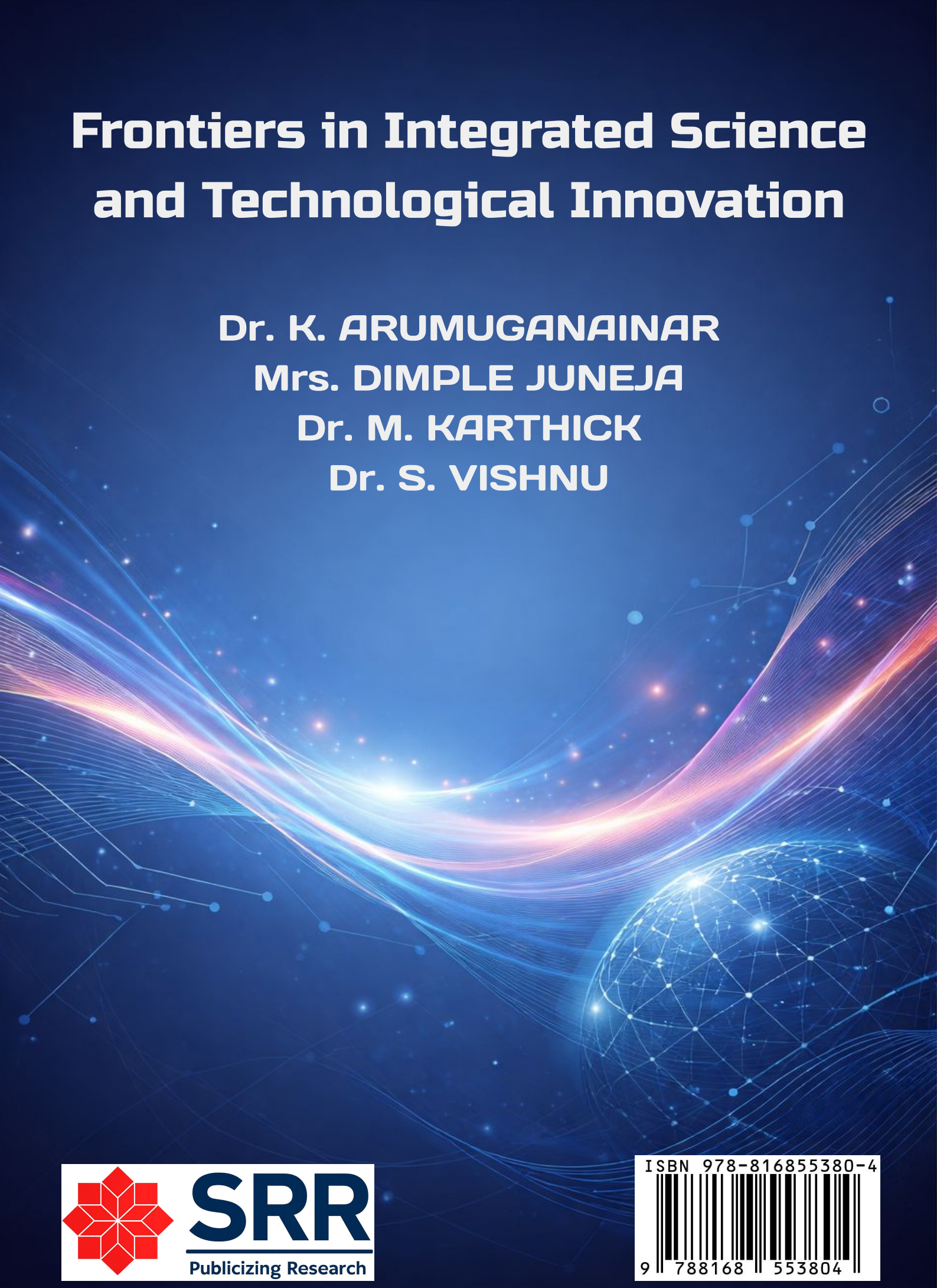

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Chapter 3

Synthesis, Growth, Structural, Optical Assessments and Second Order NLO Studies of D-Phenylglycinium Derivatives for Optoelectronic Applications

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Abstract

The domain of nonlinear optics is witnessing considerable expansion, incorporating knowledge from multiple scientific areas, such as physics, chemistry, optics, crystal growth, optoelectronics, and engineering. The study of nonlinear optics garners significant attention in organic-inorganic blend compounds, owing to their diverse properties that find applications in various fields. In-depth investigations have concentrated on the non-linear optical characteristics of organic and semi-organic crystals, which hold promising applications in device fabrication. A single crystal of D-phenylglycine derivatives, including Bis(D-phenylglycinium) sulfate monohydrate (BDPGS) and D-phenylglycine hydrochloride (DPGCL), were synthesized and grown through the slow evaporation method utilizing water as a solvent. The single crystal XRD analysis demonstrated that BDPGS crystallizes in the monoclinic space group $P2_1$, while DPGCL crystallizes in the orthorhombic space group $P2_12_12$. The optical properties of the compounds were characterized through UV-Visible absorption and reflectance spectra, revealing cut-off wavelengths of 230 nm and 228 nm for BDPGS and DPGCL,

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respectively. This indicates a bandgap of 5.4 eV, suggesting superior optical quality for potential applications. The notably low Urbach energy indicates that the crystal is nearly devoid of defects, thereby maintaining its structural integrity and evaluation of refractive index demonstrated the compounds' promising optical behavior. The effectiveness of the second harmonic generation for the synthesized crystals was clearly demonstrated using the Kurtz Perry powder method, validating both the crystals shows tremendous potential for advanced technological applications.

Keywords: Slow evaporation method, X-ray diffraction, Structural, Optical bandgap, Nonlinear analysis.

1. Introduction

The prevalence of blended materials is rapidly rising, driven by their diverse and impactful applications in fields such as medicine, industry, and materials science. These innovative materials are characterized by their conjugate structures, efficiency, and remarkable chemical adaptability, which bestow exceptional electrical, magnetic, and optical properties [1]. The realm of nonlinear optics is particularly captivated by organic-inorganic blend compounds, owing to their versatility and wide-ranging applicability across various sectors [2]. Extensive research has examined organic and semi-organic crystals' non-linear optical (NLO) properties, highlighting their potential for integration in advanced device fabrication. These crystals offer advantages such as swift response times and high damage thresholds, making them indispensable in modern technology. Notably, organic crystals are exceptionally significant for NLO applications, often showcasing efficiency levels surpassing traditional potassium dihydrogen phosphate (KDP)

crystals [3]. D-Phenylglycine, an aromatic mono-amino carboxylic acid, is distinguished by the presence of a nonpolar group in its side chain, which includes a benzene ring that contributes to its remarkable properties. This compound is a promising precursor in synthesizing semi-synthetic penicillin's and cephalosporins [4]. Recent investigative studies have delved into using phenylglycine derivatives in developing cutting-edge antitumor medications and their effectiveness in mitigating inflammation. Additionally, emerging research suggests their valuable role in enhancing the delivery and absorption of L-DOPA, a crucial therapeutic agent for various medical conditions [5]. This amino acid is not only fascinating in its own right but also acts as a vital precursor in the synthesis of β-lactam antibiotics, such as semisynthetic cephalosporins and penicillin's [6]. Derivatives of D-phenylglycine, including D-phenylglycinium bromide [7], D-phenylglycinium nitrate [8], and D-phenylglycinium perchlorate [9], are currently under intense research due to their interesting physical and chemical properties. In this exciting context, we have embarked on a significant research initiative to grow high-quality non-linear optical single crystals of D-phenylglycine derivatives such as Bis(D-phenylglycinium) sulfate monohydrate (BDPGS) and D-phenylglycine hydrochloride (DPGCL). This synthesis employs a low-temperature solution growth technique, utilizing water as the solvent at ambient temperature. Therefore, our current investigation aims to elucidate key characteristics, including single-crystal X-ray diffraction, UV-Vis transmittance and reflectance studies, and studies on optical parameters such as Urbach energy, steepness parameter, refractive index and SHG studies. This process not only demonstrates the potential of D-phenylglycine derivatives

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but also supports further research and applications in advanced optical technologies.

2. Experimental Procedure

2.1 Synthesis and growth of BDPGS

The synthesizing of the sulfuric acid admixture D-Phenylglycinium was meticulously executed by first dissolving high-purity D-Phenylglycine in concentrated sulfuric acid within a carefully measured volume of distilled water. This was performed following a precise stoichiometric ratio of 2:1. The solution was gently stirred for eight hours at a stable temperature of 35°C to achieve a uniform mixture, promoting complete solubility and homogeneity. Once the solution reached the desired consistency, it was filtered through Whatman filter paper, ensuring the removal of any impurities, and transferred into a thoroughly cleaned beaker. This beaker was then covered with a polythene sheet adorned with numerous small perforations, facilitating a controlled and gradual evaporation process. After three weeks, the slow and methodical evaporation yielded an exquisite, transparent single crystal of Bis (D-Phenylglycinium) Sulphate Monohydrate (BDPGS), as shown in Figure 1a.

2.2 Synthesis and growth of DPGCL

To prepare a concentrated solution, D-phenylglycine was carefully mixed with hydrochloric acid in a precise 1:1 ratio and dissolved in distilled water at 35°C. The mixture was then stirred vigorously for six hours to ensure a uniform and homogeneous solution. After thorough mixing, the solution was filtered through Whatman filter paper to remove any impurities. It was then placed in a controlled environment free from mechanical disturbances and thermal

vibrations, allowing the process to proceed naturally. Over several days, the slow and methodical evaporation yielded an exquisite, transparent single crystal of D-phenylglycine hydrochloride, as shown in Figure 1b.

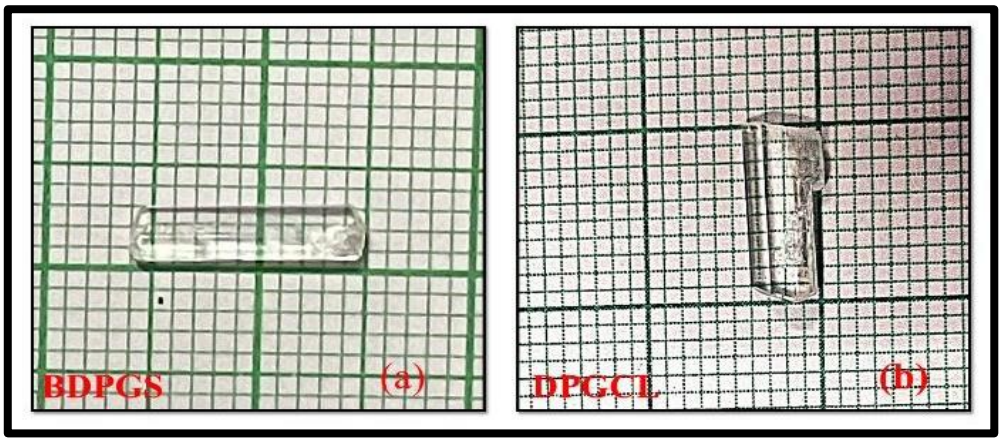

Figure. 1: As grown single crystals of (a) BDPGS (b) DPGCL

3. Results and Discussion

3.1 Single Crystal X-Ray Diffraction Analysis

Table 1. Single-crystal XRD parameters of BDPGS and DPGCL

Lattice Parameters	**Present Work (BDPGS)**	**N. Srinivasan et al. [10]**
a (Å)	12.328(3)	12.3201(12)
b (Å)	5.936(12)	5.9377(15)
c (Å)	14.296(3)	14.2908(16)
α = γ (°)	90	90
β (°)	111.335 (11)	111.369(10)
Crystal System	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1$
Lattice Parameters	**Present Work (DPGCL)**	**S. Ravichandran et al. [11]**
a (Å)	5.452(17)	5.437(5)
b (Å)	7.278(2)	7.257(8)
c (Å)	22.819(1)	22.773(2)
α = β = γ (°)	90	90
Crystal System	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$

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The Brucker D8 Quest SCXRD, which utilizes Mo-Kα radiation at ambient temperature, was employed to meticulously investigate and determine the cell parameters of the synthesized crystals of BDPGS and DPGCL. The lattice parameters for this intriguing material are measured, and notably, these values correlate strongly with those previously reported in the literature [10,11], underscoring the reliability of the synthesis and characterization process, as tabulated in Table 1.

3.2 Optical Studies

3.2.1 UV-Visible Absorbance Analysis

The UV-Vis analysis offers a compelling glimpse into the complex interplay between the electronic bandgap, atomic structure, and crystalline characteristics of the material. Our extensive absorption studies on the synthesized compound spanned a broad spectrum of wavelengths, from 200 to 800 nm, providing a thorough examination of its optical properties. The results detailed in Figures 2a and 2b reveal an impressive level of reflectance throughout the visible region, marking this material as an intriguing candidate for further scientific investigation [12]. Notably, Figures 2a and 2b highlight a significant cut-off wavelength at 230 nm and 228 nm for BDPGS and DPGCL, which serves as an important threshold in defining the optical features of the material. To gain deeper insights into its properties, we apply Tauc's relation (1), which serves as an essential framework for calculating the absorption coefficient:

$$(\alpha h\nu)^n = T\,(h\nu - Eg) \qquad (1)$$

In this equation, the exponent n varies based on the type of bandgap present: n=1/2 indicates a direct bandgap, while n=2 pertains to an indirect bandgap. The resulting Tauc's plot, depicted in Figures 3a

and 3b, indicates that the materials possess an optical bandgap energy of 5.4 eV. This striking revelation underscores the material's promising potential for nonlinear optical applications. Furthermore, this finding suggests that the material boasts a remarkably low concentration of defects, thus opening pathways for innovative applications in advanced photonic devices [13].

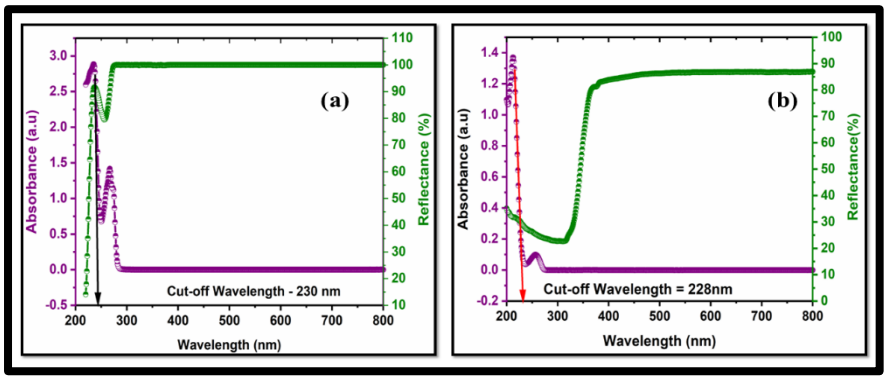

Figure 2: UV-Vis Absorbance and Reflectance spectrum of (a) BDPGS (b) DPGCL

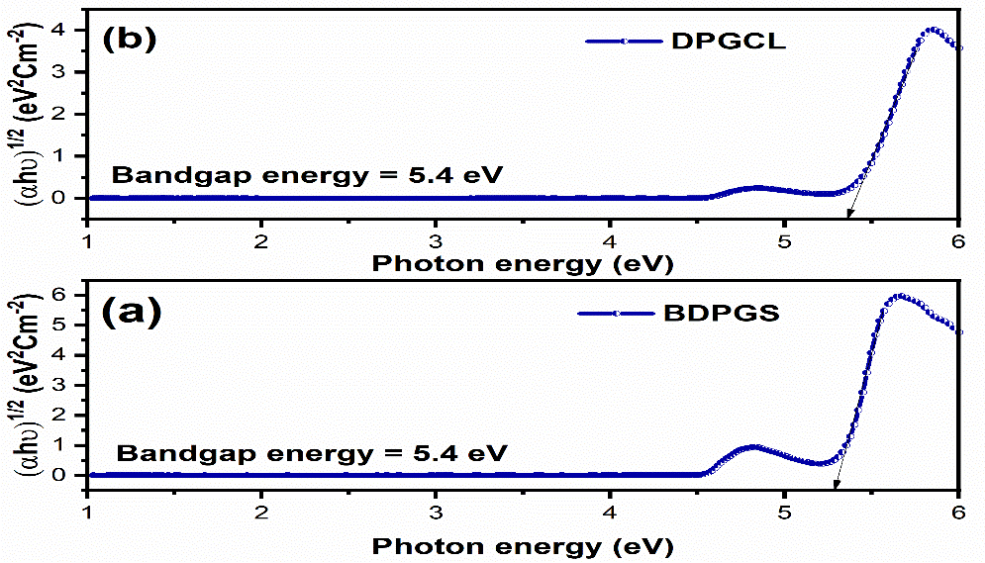

Figure 3: Bandgap Spectrum of (a) BDPGS (b) DPGCL

3.3 Absorption Band Tail

The significance of optical absorption in material science cannot be overstated, as it enables the assessment of a material's

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appropriateness for optical applications by offering vital information regarding its optical bandgap. The optical absorption spectra exhibit three distinct regions: a prominent area that denotes the optical bandgap, a subdued section that suggests the existence of flaws and impurities, and an absorption edge that illustrates variations and disruptions within the lattice structure [14]. Next to the optical bandgap on the absorption coefficient curve lies an exponential region referred to as the Urbach tail. The exponential tail, also known as Urbach energy, plays a crucial role in weakly crystalline materials and shows a notable reduction in well-crystalline specimens [15]. An exponential equation illustrates the connection between the absorption coefficient (α) and photon energy, known as the Urbach empirical rule.

$$\alpha = \alpha_o exp\left(\frac{h\nu}{E_u}\right) \qquad (2)$$

$$ln(\alpha) = ln\,(\alpha_o) + ln\frac{h\nu}{E_u} \qquad (3)$$

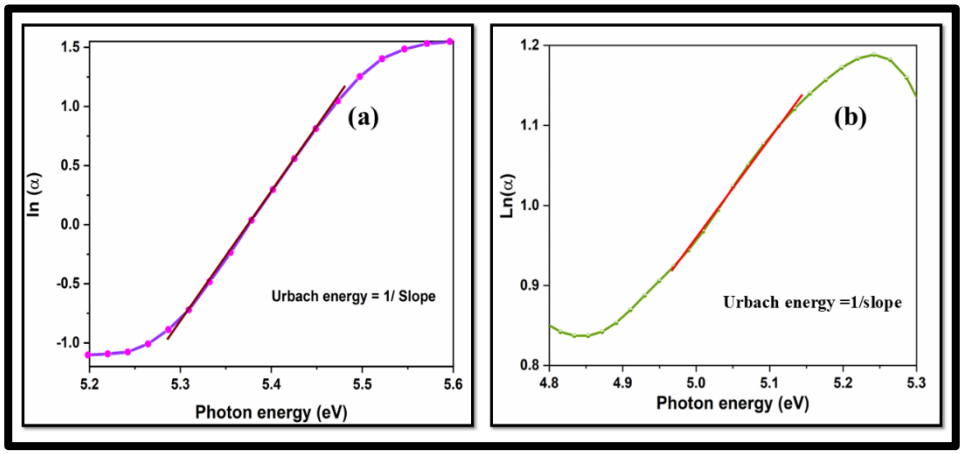

Figure 4: Plot of Photon energy (hν) vs ln (α)

In this equation, the E_U denotes the Urbach energy. The examination of the graph shown in Figures 4a and 4b, which presents photon energy against ln(α), indicates that the inverse of the slope is

associated with an Urbach energy of BDPGS and DPGCL, measured at 0.1101 eV and 0.858 eV, respectively. This observation indicates that the materials are free from imperfections and lattice disorder [16]. Additionally, Urbach identified a secondary relationship between the absorption coefficient and the optical bandgap, as detailed in equations (4-5).

$$\alpha = \beta \exp\left[\frac{\sigma(h\nu - E_o)}{K_B T}\right] \qquad (4)$$

$$\left(\frac{h\nu}{E_U}\right) = \left(\frac{\sigma(h\nu)}{K_B T}\right) \qquad (5)$$

Here, E_U is Urbach energy, K_B denotes the Boltzmann constant, and T represents the absolute temperature. The steepness parameter (σ) is determined through equation (6),

$$\sigma = \frac{K_B T}{E_U} \qquad (6)$$

Additionally, the strength of the electron-photon interaction ($E_{e\text{-}p}$) is calculated using equation (7),

$$E_{e\text{-}p} = \frac{2}{3\sigma} \qquad (7)$$

Table 2. Urbach energy and its key parameters of BDPGS and DPGCL

Description	**BDPGS**	**DPGCL**
Wavelength of absorption edge (nm)	230 nm	228 nm
Optical bandgap E_g	5.4 eV	5.4 eV
Urbach Energy E_U	0.110 eV	0.858 eV
Steepness parameter σ	0.2138	0.2742
Electron-photon interaction energy $E_{e\text{-}p}$	3.11	2.43

Table 2 summarises the values for the cut-off wavelength (nm), optical band gap energy (E_g), Urbach energy (E_U), steepness parameter (σ), and electron-photon energy ($E_{e\text{-}p}$), of BDPGS and DPGCL indicating that the materials possess exceptional

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characteristics and demonstrates significant potential for device fabrication [17].

3.4 Determination of Optical Constant

The optical constants, including optical conductivity, refractive index, and extinction coefficient, play a vital role in fabricating nonlinear optical devices. It is essential to use materials with exceptional optical quality and an excellent refractive index to develop effective devices such as optical switches and organic light-emitting diodes. The refractive index is exclusively determined by the material's composition and reflective properties [18]. According to equation (8), the refractive index can be derived from reflectance measurements.

$$n = \frac{-(R+1) \pm \sqrt{(-3R^2+10R-3)}}{2(R-1)} \qquad (8)$$

The plot presented in Figure. 5a and 5b demonstrates that the materials refractive index is measured to be 1.370 and 1371 for BDPGS and DPGCL at a wavelength of 532 nm [19].

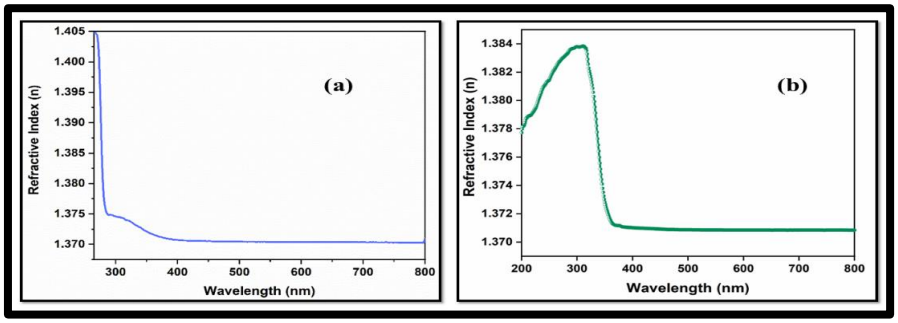

Figure 5: Wavelength (nm) vs Refractive index (n)

The reduction in the refractive index, coupled with strong transmission across the visible spectrum, indicates that the material possesses enhanced efficiency for optical applications.

3.5 Second Order Nonlinear Optical Studies

The second-harmonic generation (SHG) conversion efficiency of the sample was carefully evaluated using the Kurtz-Perry powder technique, a widely recognised method in the field [20]. For this analysis, powdered potassium dihydrogen phosphate (KDP) served as a standard reference material, given its well-established SHG properties. A high-intensity, Q-switched Nd: YAG laser emitting a fundamental wavelength of 1064 nm was used as the optical source for the experiment.

Table 3. SHG efficiency of various semi organic material with respect to KDP

Nonlinear Optical Materials	SHG efficiency
L-Glycine thiourea [22]	0.60
Diglycine hydrobromide [23]	0.80
Thiourea urea zinc sulphate [24]	0.82
Glycine Zinc Sulfate [25]	1.20
Bis(D-Phenylglycinium) sulfate monohydrate [present study]	1.23
D-phenylglycine hydrochloride [present study]	1.35

This powerful laser is known for its effectiveness in producing nonlinear optical effects. As expected, the SHG process was confirmed by the detection of green light at 532 nm, clearly indicating the material's nonlinear optical response. At an input energy of 0.7 J, the SHG output for the BDPGS compound was 6.6 mJ and DPGCL was about 7.2 mJ, significantly exceeding the KDP reference, which recorded an output of 5.4 mJ. This notable result showed that the SHG efficiency of the BDPGS was 1.23 times and DPGCL is 1.35 times greater than that of KDP, demonstrating its superior nonlinear optical performance and is compared with other NLO materials as shown in

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Table 3. Additionally, it was observed that the SHG efficiency tends to increase with larger particle size [21], suggesting that optimising particle dimensions could lead to further improvements in SHG efficiency.

4. Conclusion

A high-quality nonlinear single crystal of Bis(D-phenylglycinium) sulphate monohydrate and D-phenylglycine hydrochloride was carefully synthesized using the solution growth method of slow evaporation, with distilled water as the solvent to guarantee purity. Thorough XRD investigations revealed that the crystal BDPGS features a notable monoclinic structure, classified under the space group $P2_1$, while DPGCL exhibits an orthorhombic system with the space group $P2_12_12$, highlighting its distinctive crystalline arrangement. The optical properties of the crystals were clarified, revealing a lower cutoff wavelength of 230 nm for BDPGS and 228 nm for DPGCL, which corresponds to a notable bandgap energy of 5.4 eV. The exceptionally low Urbach energy indicates that the crystal is nearly devoid of defects, thereby maintaining its structural integrity and evaluation of refractive index demonstrated its encouraging optical characteristics. The effectiveness of the second harmonic generation for the synthesized crystal of BDPGS and DPGCL was clearly demonstrated using the Kurtz method, affirming its diverse potential for advanced technological applications.

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