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Growth, optical and dielectric studies of glycine doped ammonium dihydrogen phosphate nlo crystal: potential material for optoelectronics applications

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Abstract

The 3 mole% glycine doped ADP crystal was grown by slow evaporation technique at ambient temperature. The incorporation of glycine was analyzed qualitatively by FT-IR analysis. The grown crystal exhibits high transmittance in the entire visible region and lower cut-off wavelength has been found to be 306 nm. The optical band gap is found to be 5 eV. The high optical quality of the grown crystal was ascertained by lower values of extinction coefficient (k) and refractive index (n). The dielectric constant and the dielectric loss decreases with the increasing frequency. Thermal studies of the grown crystal confirmed its stability up to 205 °C. The relative SHG efficiency for 3 mole% glycine doped ADP was measured using Nd:YAG laser and the value observed to be 1.88 times that of pure ADP.

Keywords: crystal growth, growth from solution, optical properties, dielectric properties, SHG efficiency

1. Introduction

The search for materials possessing high optical nonlinearity is an important task because of their practical applications in harmonic generation, optical communication, data storage, switching and other optical switching devices [1–5]. Ammonium dihydrogen phosphate (ADP) crystals have a wide range of applications in integrated and nonlinear optics because of their

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piezo-electric (antiferroelectric at low temperature) and nonlinear optical properties. Due to their interesting electrical and optical properties, structural phase transitions and ease of crystallization, they has been the subject of a wide variety of investigations for several years. Amino acids play an important role in the field of non-linearity. Among them glycine with chemical formula ($C_5H_5NO_2$) is the simplest, naturally possessing the chiral amino acid. Many researchers have carried out studies in pure and doped ADP [6–9]. Ferdousi *et al* [10] reported the structural, optical, thermal and electrical properties of L-Alanine doped ADP crystal. Rajesh *et al* [11] reported growth and characterizations of D_L-malik acid doped with ADP. Pattanaboonmee *et al* [12] reported the comparative studies of pure and 1 mole% L-arginine and glycine doped ADP crystal by slow solvent evaporation and Sankaranaranyanan–Ramasamy (SR) method. However, the SHG efficiency and optical parameters of glycine doped ADP crystal have not been reported, which is the key factor for NLO applications. Hence, in the present communication, NLO studies and the optical parameters such as optical band gap, refractive index, and extinction coefficient are reported and the findings are going to provide useful data for fabrication of optoelectronics devices and NLO applications. The grown crystal was characterized by powder XRD, FT-IR, thermal analysis, optical and dielectric studies and the results were compared with pure ADP crystal.

2. Experimental procedure

The analytical grade reagent samples of pure ADP and 1, 2 and 3 mole% glycine doped ADP were dissolved in molar ratio 1:1:2:3 in double-distilled water, respectively. The solution was constantly stirred using a magnetic stirrer at a constant rate for six hours to get homogeneity. The prepared solutions were then filtered twice; the purity of the salts was achieved by repetitive recrystallisation, good quality transparent seed crystals were harvested within 4–5 days by slow evaporation method. The transparent and well-defined shaped seed crystal was selected to grow bulk crystal. The seed crystal was suspended in super saturated solution of 3 mole% glycine doped ADP at 32 °C in constant temperature bath having an accuracy of ±0.01 °C. The bulk crystal of 3 mole% glycine doped ADP with dimension $3.5 \times 1.3 \times 1.2$ cm was grown in two weeks and is shown in figure 1.

3. Results and discussion

3.1. X-ray diffraction analysis

The grown crystal was subjected to powder XRD, the unit cell parameters obtained are $a = b = 7.503$ A° and $c = 7.556$ A° $\alpha = \beta = \gamma = 90°$. The obtained lattice parameter values confirmed that the addition of glycine did not changed the tetragonal structure of ADP [12].

3.2. FT-IR analysis

FT-IR spectrum recorded in the range of 450–4000 cm^{-1} employing a Perkin Elmer Spectrum FTIR spectrometer by KBr pellet technique is shown in figure 2. The peaks at 3105 cm^{-1} may be assigned to N–H stretching vibrations. The symmetric and asymmetric stretching modes of COO- are seen at 1580, 1480, 1405 and 1323 cm^{-1}. This observation confirms that glycine can exist in zwitterionic form. The C–H and O–H bond of the COOH group are observed at 1238,

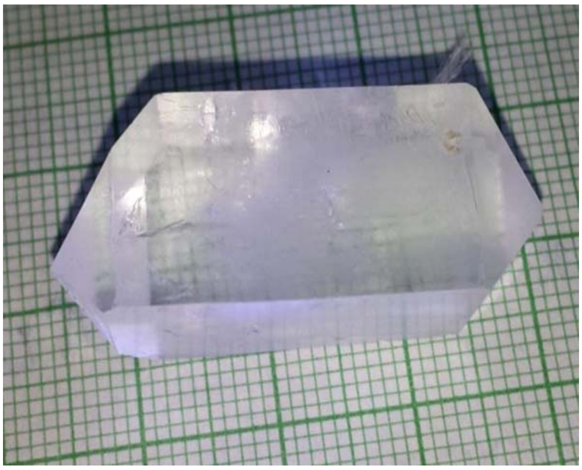

Figure 1. Photograph of grown 3 mole% glycine doped ADP crystal.

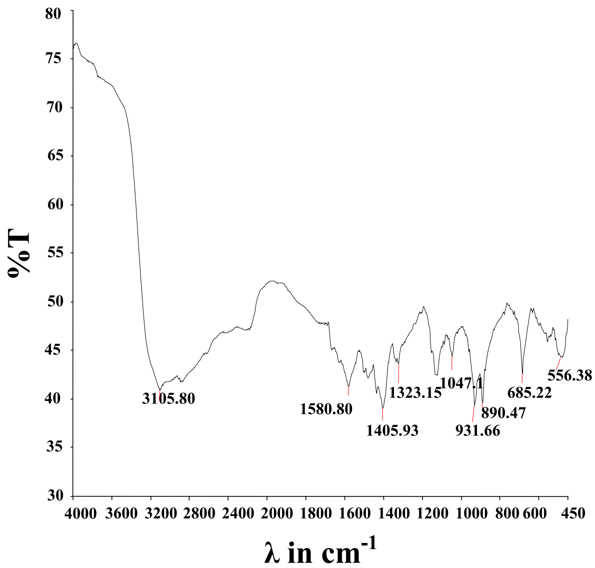

Figure 2. FTIR Spectrum of 3 mole% glycine doped ADP.

1308 and 1349 cm^{-1}, respectively. The PO_4 vibration peaks at 556.38 cm^{-1} and 685.22 cm^{-1}. All these observations demonstrate the existence of glycine in its salt form with ADP [13].

3.3. SHG (NLO) studies

The Kurtz and Perry powder SHG test was performed at Indian Institute of Science (IISc), Bangalore, India; the pure and 1, 2, 3 mole% glycine doped ADP crystals were powdered and illuminated by Nd:YAG laser with first harmonics output of 1064 nm, width 8 ns and repetition rate 10 Hz. The input laser energy incident on sample was 2.8 mJ. The output signals obtained for pure and 3 mole% glycine doped ADP are 72 mV and 135 mV, respectively, thus the result obtained for 3 mole% glycine doped ADP shows a powder SHG efficiency of about 1.88 times that of pure ADP. This increase in SHG of ADP with addition of glycine is due to the fact that glycine is an optically active material and possesses Zwitter ion, which is connected with ADP

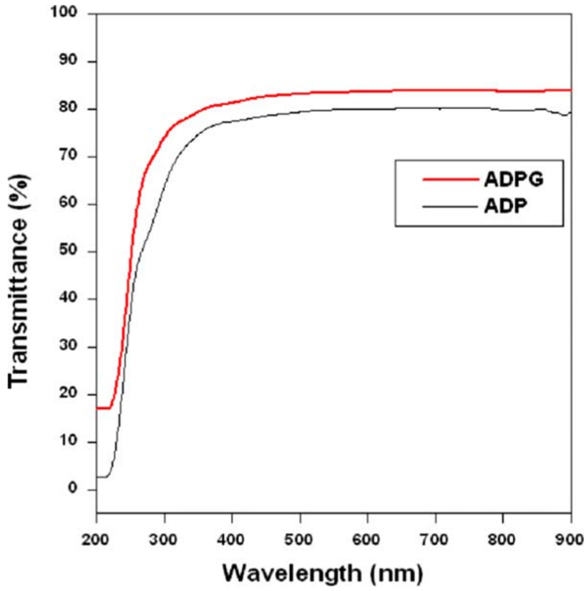

Figure 3. UV-Vis. Spectrum of 3 mole%.

by short O–H–O hydrogen bonds. Glycine has more dipole moment due to the presence of polar NH_3 amino group [14].

3.4. Optical studies

The optical parameters of a material are important as they provide information on the electronic band structures, localized states and types of optical transitions. The optical studies for pure and doped ADP crystals were carried out using a Shimadzu UV-2450 Spectrophotometer in the range 200–900 nm. Figure 3 shows the transmittance spectra of the grown crystal. The lower cut-off wavelength is found to be 306 nm. The high transmission in the entire visible region suggests its suitability for second harmonic generation; very low transmittance in UV region makes the grown glycine doped ADP crystal a potential candidate for use as an effective UV shelter [15]. The measured transmittance (T) data was used to calculate absorption coefficient (α) from the following relation:

$A = (1/t)\ \ln\ (1/T)$; where T is the transmittance and t is the thickness of the crystal. Optical band gap (Eg) was evaluated from the transmission spectrum and optical absorption coefficient (α) near the absorption edge is given by: $\alpha h\nu = A\ (h\nu - E_g)^{1/2}$ where Eg is the optical band gap of the crystal and A is a constant.

The band gap of glycine doped ADP was calculated by extrapolation of the linear portion of the curve as shown in figure 4. The band gap of 3 mole% glycine doped ADP was found to be 5 eV. The wide band gap of glycine doped ADP crystal makes it a potential candidate for optoelectronic applications [16].

Extinction coefficient can be obtained by the relation, $K = \alpha\lambda/4\pi$ and is shown in figure 5. The refractive index (n) is calculated using the relation as given by Bakr *et al* [17] and shown in figure 6. The lower values of extinction coefficient and refractive index of doped ADP in entire visible region substantiates its suitability for antireflection coating in solar thermal devices and optical fabrication [18, 19].

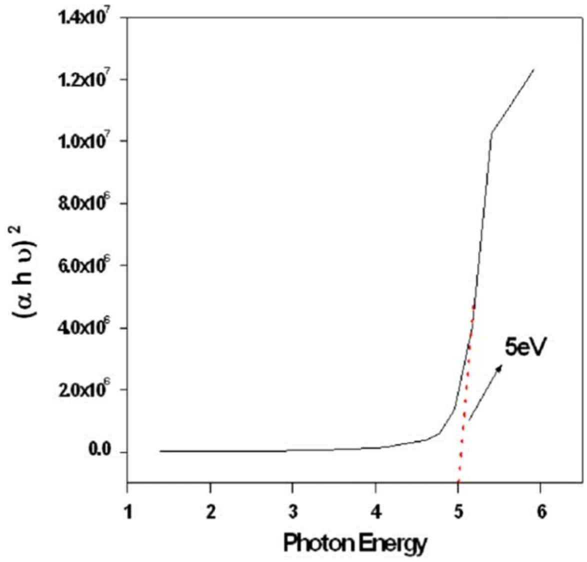

Figure 4. $(\alpha h\nu)^2$ versus photon energy $(h\nu)$ glycine doped ADP.

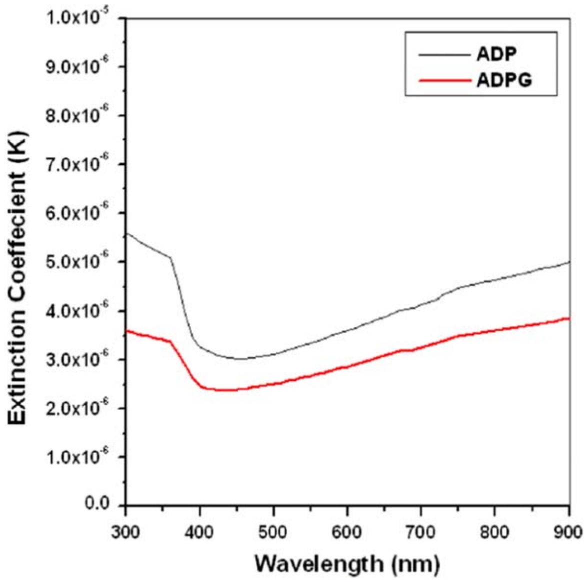

Figure 5. Plot of extinction coefficient versus Wavelength.

3.5. Dielectric studies

Dielectric studies were carried using the LCR-819 series, Gwinstek instrument having frequency range of 10 Hz to100 kHz. The dielectric constant was calculated using the formula $\varepsilon = C\ d/\varepsilon_o A$ Where C is the capacitance, d is the thickness of the sample; A is the area of the sample. Dielectric loss was calculated using the formula, Tan $\delta = \varepsilon/\varepsilon_0$. The plot of dielectric constant and dielectric loss are shown in figures 7 and 8, respectively.

The increasing dielectric constant at low frequencies may be due to the presence of all the four polarizations, namely space charge, orientation, electronic and ionic polarization. The decrease in dielectric constants at higher frequencies is attributed to the significant decrease in

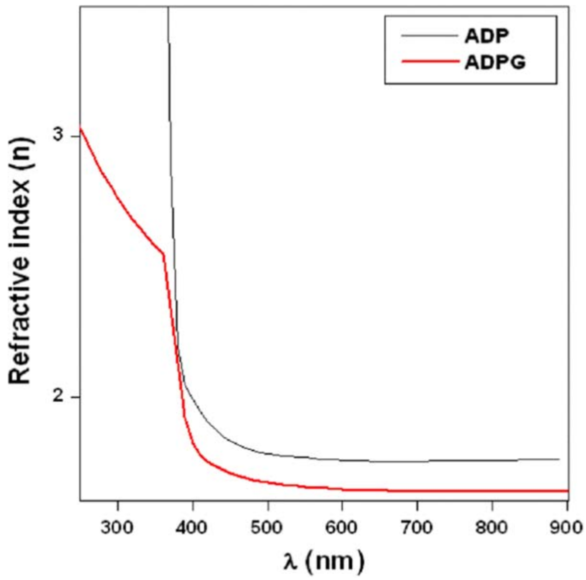

Figure 6. Plot of refractive index versus wavelength.

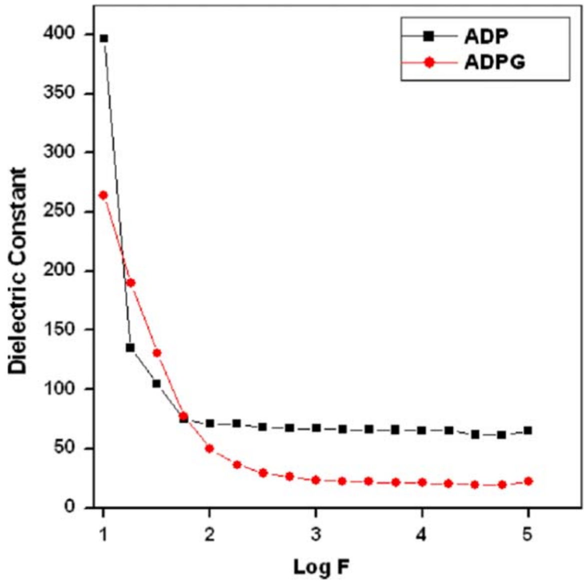

Figure 7. Plot of dielectric constant versus Log F.

these polarizations and absence of space charge polarization near the grain boundary interface [20]. The lower dielectric constant at higher frequencies is an essential parameter for enhancing the SHG coefficient of material [21]. The NLO applications demands low dielectric constant and dielectric loss. Figure 8 depicts that glycine doped ADP crystal has low dielectric loss at high frequencies which proves that grown crystal possesses enhanced optical quality with fewer defects suggesting its suitability for NLO device fabrication [21].

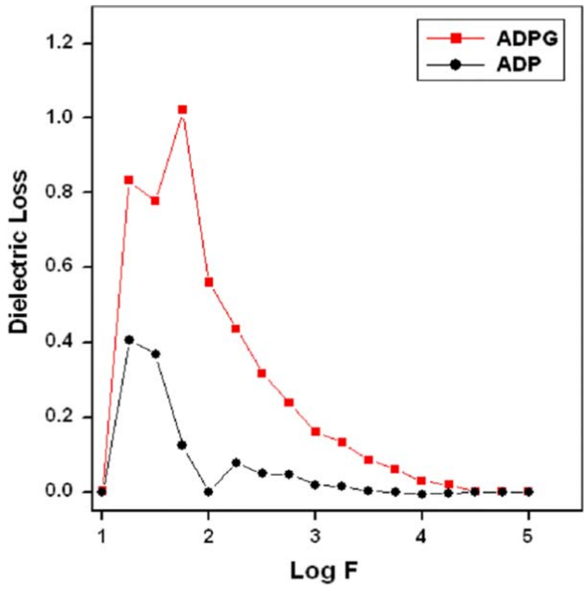

Figure 8. Plot of dielectric loss versus Log F.

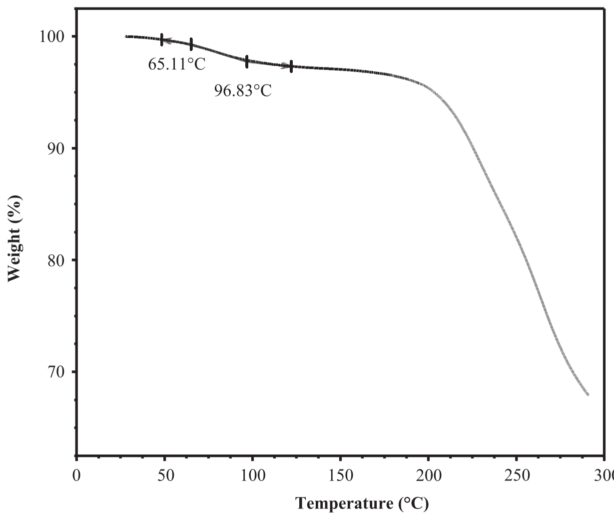

Figure 9. TGA Thermogram.

3.6. Thermogravimetric analysis

The 3 mole% glycine doped ADP crystal was subjected to thermo gravimetric analysis (TGA) using TAQ-500 and thermo gravimetric analyzer at a heating rate of 25 °C min^{-1} to 300 °C in nitrogen inert atmosphere to determine the change in thermal stability of ADP after incorporation of glycine. The TGA curve exhibits negligible weight loss from 40 °C up to 200 °C and stable at 205 °C as shown in figure 9. The weight loss from 210 to 300 °C may be due to decomposition of ADP and glycine [12].

4. Conclusion

3 mole% glycine doped ADP crystal was successfully grown by employing the slow evaporation method. The powder XRD confirmed the tetragonal symmetry of the crystal. The FT-IR spectra confirmed the incorporation of glycine in the material of grown crystal. The SHG efficiency of 3 mole% glycine doped ADP crystal is 1.88 times that of pure ADP. The optical study confirmed high optical transparency. The optical band gap was found to be 5 eV with improved optical constants suggesting its suitability for NLO applications. Dielectric studies ascertained that the grown crystal possesses low dielectric loss and dielectric constant which is highly demanded for the fabrication of optoelectronic devices. TGA analysis revealed that the grown crystal was stable up to 205 °C. All the above studies of the grown glycine doped ADP crystal confirmed it is a potential material for various optoelectronic applications.

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Page 8

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