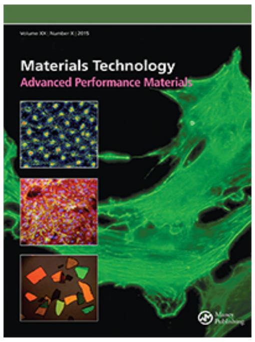

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Investigation on fluorescence, third order non-linear optical and mechanical performance of glycine doped ADP crystal for applications of photonic devices

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SHORT COMMUNICATION

Investigation on fluorescence, third order non-linear optical and mechanical performance of glycine doped ADP crystal for applications of photonic devices

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Optically transparent glycine doped ammonium dihydrogen phosphate crystals have been grown from aqueous solution by slow solution evaporation method. Crystallographic data of the grown crystal has been determined using the single crystal X-ray diffraction technique. The photoexcited colour centred fluorescence emission spectrum of the grown crystal has been analysed at an emission wavelength of 254nm in the range of 300 to 700nm. Z-scan studies have been performed at 632·8nm to confirm the negative third order non-linear refraction behaviour of the grown crystal. The non-linear refractive index (n_2), non-linear absorption coefficient (β) and third order non-linearity susceptibility (χ^3) of the grown crystal were calculated using the Z-scan data to explore the material suitability for photonic applications. Vicker's microhardness test was carried out to analyse the mechanical stability and determine the hardness parameters of the grown crystal.

Keywords: Growth from solution, Fluorescence, Z scan technique, Microhardness study

Introduction

The development of materials from nano to bulk nonlinear optical (NLO) crystals has been highly encouraged since the past two decades for integrated optics, biomedical imaging, remote sensing and photonic applications.[1–5] One of the potential oxide crystals, the ammonium dihydrogen phosphate (ADP) crystal, interests many researchers as it exhibits large non-linear response, high optical homogeneity and strong electro-optic property, which enables its utility for large scale industrial photonic devices that include high speed optical data modulation, laser frequency conversion, optical switching, parametric mixing and optoelectronic applications.[6–8] In order to improve the characteristic properties of this industrially vital ADP crystal, many researchers have encouraged use of organic dopants containing donor–acceptor groups to improve its overall performance for imparting it to fabricate more efficient NLO devices.[9] Owing to this donor–acceptor charge transfer tendency, amino acids offer excellent electro-optical and thermo-mechanical properties to inorganic host crystal. Evidently, use of amino acids such as L-alanine, L-proline, L-arginine, L-lysine and glycine has been a successful attempt to enhance the SHG coefficient, laser damage threshold, optical, mechanical and dielectric properties of ADP crystal.[10–14] The NLO and photonics application demands a material with promising fluorescence, third order non-linear optical and mechanical properties, which are not explored in case of glycine doped ADP crystal. Hence, in present communication for the very first time, the third order non-linear optical, fluorescence and mechanical properties of glycine doped ADP crystal has been investigated to explore its utility for designing NLO devices.

Experimental

Analytical grade glycine was added in three different mol.-% viz. 1, 2 and 3 in the supersaturated solution of ADP. The solutions were allowed to stir separately with constant speed on the magnetic stirrer for 6 h to achieve homogeneity throughout the volume. The solutions were then filtered and kept for slow evaporation at room temperature. The good quality transparent seed crystals were harvested within 4 to 5 days by slow evaporation method. The salts of these three different mol.-% glycine doped ADPs were subjected to SHG test, and the highest SHG efficiency was observed in 3 mol.-% glycine doped ADP. Hence, the bulk crystal of 3 mol.-% glycine doped ADP was grown by slow evaporation at 32 °C temperature. The as grown glycine doped ADP crystals are shown in Fig. 1.

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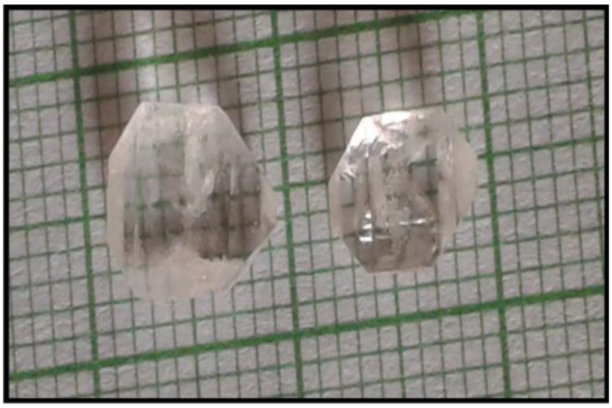


1 Photograph of grown crystal

Results and discussion

Single crystal X-ray diffraction analysis

The cell parameters of the grown crystal have been determined at room temperature using an Enraf Nonius CAD-4 crystal X-ray diffractometer. It is observed that the grown crystal belongs to the tetragonal symmetry, and the determined unit cell parameters are discussed in Table 1. It is evident that the incorporation of glycine did not alter the tetragonal structure of ADP crystal but definitely caused a slight change in cell parameters.[12]

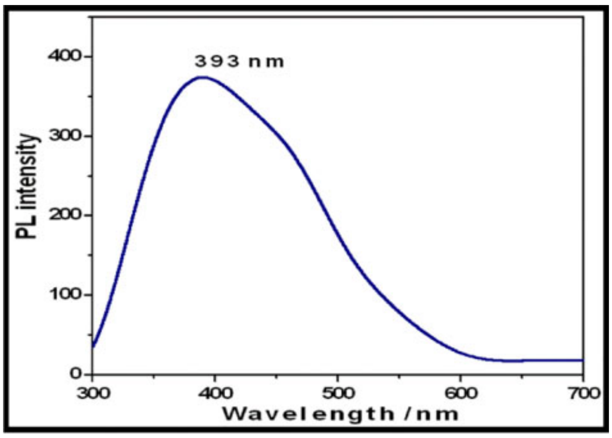
Optical studies

Fluorescence study

Fluorescence study of grown crystal was performed in the visible range of 300 to 700 nm using a HIOKI 3540 spectrophotometer at room temperature. The optical emission behaviour of the material is an essential parameter in the field of biochemical, medical and chemical researches to assess the surfaces, interfaces and impurity levels and to probe the alloy disorder and interface roughness.[15] The emission spectra of the grown crystal shown in Fig. 2 enable to analyse the electronic transition occurring due to the absorption of light by intrinsic impurities causing colour centred emissions. The emission behaviour of grown crystal has been investigated at 254 nm, and it showed a single prominent violet emission peak centred at 393 nm in the visible region. The single emission with no shoulder peaks evidences the superior quality of the crystal material, which is substantial for NLO applications.[16]

Table 1 X-ray diffraction data

Crystal	Crystal system	Cell parameters/Å	Volume/(Å)^3
ADP	Tetragonal	$a=b=7{\cdot}51$, $c=7{\cdot}56$	426
Doped ADP	Tetragonal	$a=b=7{\cdot}5$, $c=7{\cdot}55$	424



2 Photoluminescence emission spectrum

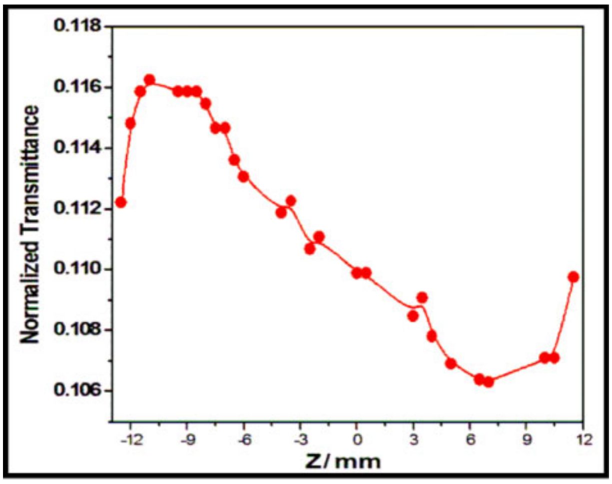
Z scan studies

The Z scan analysis is an important tool to investigate the third order non-linear behaviour of crystal system at single wavelength and find its possible applications for photonics applications, such as optical signal processing, optical communication, optical computing and optical limiting effect.[17] In closed aperture Z scan study, the polarised beam of He–Ne laser ($\lambda = 632{\cdot}8$ nm) was normally focused on the crystal sample through the lens of focal length 12 cm, and the crystal was gradually translated about the focus (Z = 0) along the Z direction, and the transmittance was recorded using the photo detector placed at a far field. This systematic measurement of transmittance helps to determine the nature and magnitude of refractive non-linearity of the crystal material.[14] The close aperture Z scan curve (Fig. 3) resembles the negative refraction non-linearity as a prefocus peak is followed by a post-focus valley, which is the characteristic property of material exhibiting the self-defocusing effect.[18]

The origin of refraction non-linearity is due to the spacial distribution of energy along the crystal surface caused by localised absorption of highly repetitive incident optical field.[19] The negative phase shift in refraction non-linearity suggests the suitability of the grown crystal for protection of optical night vision sensor devices.[20] The magnitude of non-linear refraction is found to be $4{\cdot}55\times10^{-13}$ cm^2 W^{-1}. The peak to valley transmission difference in terms of phase shift is given as

$$\Delta T_{p-v} = 0{\cdot}406(1-S)^{0{\cdot}25}|\Delta\phi| \quad (1)$$

where $S=[1-\exp(-2r_a^2/\omega_a^2)]$ is the aperture linear transmittance, r_a is the aperture radius and ω_a is the beam radius at the aperture. The non-linear refractive index was calculated as[14]



3 Closed aperture Z scan curve

$$n_2 = \frac{\Delta\phi}{KI_0L_{\text{eff}}} \quad (2)$$

where $K = 2\pi/\lambda$, I_0 is the intensity of the laser beam at the focus $Z = 0$, $L_{\text{eff}} = [1-\exp(-\alpha L)]/\alpha$ is the effective thickness of the sample depending on linear absorption coefficient (α) and L is the thickness of the sample. The non-linear absorption coefficient (β) of the grown crystal has been evaluated using the open aperture transmittance curve (Fig. 4) evaluating the equation shown below[14]

$$\beta = \frac{2(2)^{1/2}\Delta T}{I_0L_{\text{eff}}} \quad (3)$$

The third order non-linear susceptibility of grown crystal was calculated using the relations depicted below[17]

$$\text{Re}\,\chi^{(3)}(\text{esu}) = 10^{-4}(\varepsilon_0 C^2 n_0{}^2 n_2)/\pi(\text{cm}^2\ \text{W}^{-1}) \quad (4)$$

$$\text{Im}\,\chi^{(3)}(\text{esu}) = 10^{-2}(\varepsilon_0 C^2 n_0{}^2 \lambda\beta)/4\pi^2(\text{cm}\ \text{W}^{-1}) \quad (5)$$

$$\chi^3 = \left[(\text{Re}\,\chi^3)^2 + (\text{Im}\,\chi^3)^2\right]^{1/2} \quad (6)$$

where ε_0 is the vacuum permittivity, n_0 is the linear refractive index of the sample and c is the velocity of light in vacuum. The open aperture curve confirms the phenomenon of saturable absorption that originated as ground state linear absorption overpowers the absorption offered by the excited state.[21] The non-linear absorption coefficient (β) of the grown crystal is found to be $5{\cdot}26\times10^{-7}$ cm W^{-1}. The cubic susceptibility (χ^3) of the grown crystal is found to be $4{\cdot}84\times10^{-6}$ esu, which is notably greater than the reported crystals.[19] The figure of merit can be evaluated using the relation ($\beta\lambda/n_2$). The figure of merit value of the grown crystal is found to be 0·73, indicating its suitability for photonic applications.[22] The third order NLO properties of the grown crystal are discussed in Table 2. The promising NLO properties of the grown crystal suggest its suitability for applications of optical limiting, optical logic gates, passive laser modelocking and waveguide switching devices.[23]

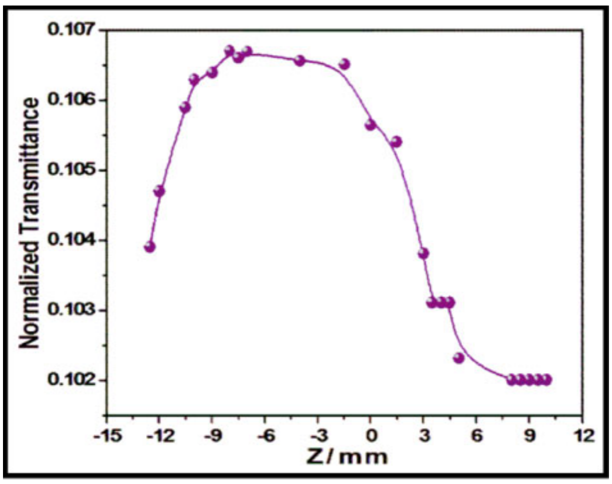
Microhardness study

To find the surface hardness of the grown crystal, microhardness studies were performed by employing different loads (10 to 50 g) using the Vicker's microhardness tester. The indentation period was fixed as 10 s for each trial. Repeated trials were performed to ascertain the correctness of the observed result. The Vicker's hardness number (H_v) was calculated using the standard formula: $H_v = 1{\cdot}8544\ p/d^2$, where p is the applied load in kilogram, and d is the mean diagonal length of the indention in millimetre. The variation of hardness number with load is depicted in Fig. 5. The hardness value is observed to be decreasing with the increase in load, satisfying the normal indentation size effect.[24] These results indicate that the glycine doped ADP crystal has moderate hardness quality, which justifies its usability for device applications. It is noteworthy that the glycine doped ADP crystal has superior hardness than 1 mol.-% L-alanine doped ADP crystals.[9] The work hardening index of the grown crystal was calculated using Meyer's law, which relates the load and indention diagonal length as $P{=}k.d^n$, where k is the material constant, and n is Meyer's index.

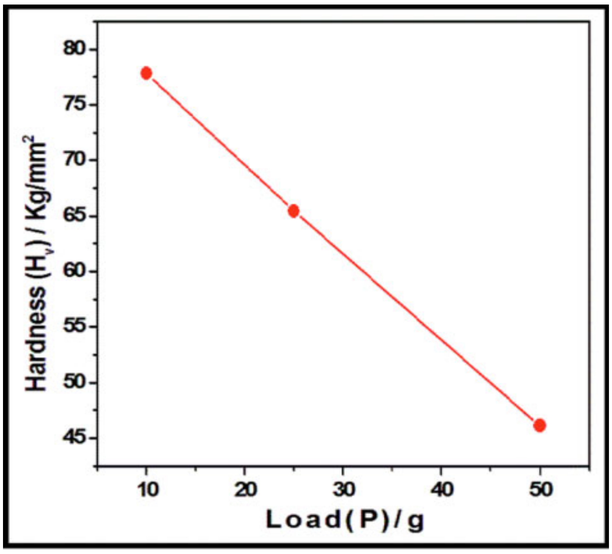
In order to find the value of 'n, a graph is plotted between log P and log d (Fig. 6), which gives a straight line, and it is found to be 1·68. According to the Onitsch criterion, the calculated value of n suggests that the grown crystal belongs to the category of soft materials.[25] For designing the NLO device components, it is important to tailor the hardness parameters of the grown crystal. The yield strength (σ_y) of the grown crystal was calculated using the relation $\sigma_y = (0{\cdot}1)^{n-2}H_v/3$.[26] According to the relation, the yield

Table 2 Measurement details and results of Z scan technique

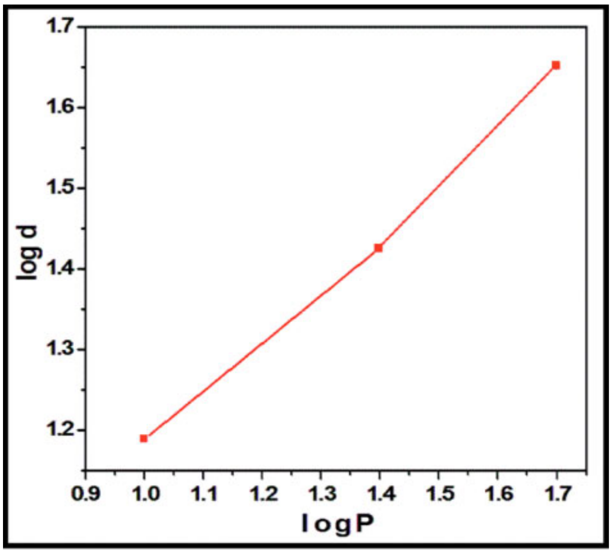
Laser beam wavelength/λ	632·8 nm
Optical path distance/Z	115 cm
Spot size diameter in front of the aperture/ω_a	1 cm
Aperture radius/r_a	4 mm
Incident intensity at the focus/$Z = 0$	3·13 MW cm^{-2}
Effective thickness L_{eff}	1·83 mm
Non-linear refractive index n_2	$-4{\cdot}55\times0^{-13}$ $cm^2\ W^{-1}$
Non-linear absorption coefficient β	$5{\cdot}26\times10^{-7}$ cm W^{-1}
Third order non-linear optical susceptibility χ^3	$4{\cdot}84\times10^{-6}$ esu



4 Open aperture Z scan curve



5 Vicker's hardness verses load



6 Plot of log *P* verses log *d*

Table 3 Hardness parameters at different loads

Sr. no.	Load/g	H_v/kg mm^{-2}	Elastic stiffness constant $C_{11}/\times 10^{14}$ Pa
1	10	77·8	34·98
2	25	65·4	25·81
3	50	46·1	13·99

strength was found to be 489 MPa. The relation between the elastic stiffness constant ($C_{11} = H_V^{7/4}$) and the hardness number is given by Wooster's empirical formula.[27] The evaluation of the elastic stiffness constant provides information about the strength of bonding between neighboring atoms. The calculated elastic stiffness constant for different loads is given in Table 3. The elastic stiffness constant of the grown crystal shows relative decrease with increase in load, confirming the appreciable binding forces between the consecutive ions.

Conclusion

Optically transparent glycine doped ADP crystals have been grown by slow solution evaporation technique. X-ray diffraction analysis confirmed the slight change in cell parameters and tetragonal structure of glycine doped ADP crystal. Microhardness analysis reveals that the grown crystal belongs to the category of soft materials, and it obeys the normal indentation size effect. The fluorescence study revealed the single prominent violet coloured emission peak centred at 394 nm. Z scan analysis confirmed the effective third order non-linear behaviour at 632·8 nm. The grown crystal exhibits negative refraction non-linearity with magnitude of $-4{\cdot}55\times10^{-13}$ cm^2 W^{-1}. The cubic susceptibility of order 10^{-6} esu confirms the strong polarising nature and enhanced π electron charge transfer module of the grown crystal. The above studies conclude that the glycine doped ADP crystal could be advantageous for applications of various frontier technological photonic devices utilised in optical limiting systems, night vision sensors, optical logic gates, optical switching, signaling and modulating systems.

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