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Effect of L-cysteine on optical, thermal and mechanical properties of ADP crystal for NLO application

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ABSTRACT

The ammonium dihydrogen phosphate (ADP) crystal doped with amino acid L-cysteine (LC) was grown by a slow evaporation technique. The grown crystal was transparent in the entire visible region, which is an essential requirement for a nonlinear crystal. The LC doping enhances the optical band gap of ADP (5.35 eV). The TG/DTA analysis of LC doped ADP crystal confirms the optimum thermal stability of grown crystal. The enhancement in the mechanical stability after LC doping was confirmed by Vicker's microhardness test. The LC doping showed significant impact on dielectric properties (dielectric constant and dielectric loss) of grown crystal. The third order nonlinear behavior of LC doped ADP crystal was investigated using a *Z*-scan technique at 632.8 nm and effective nonlinear optical parameters were evaluated.

1. Introduction

The ammonium dihydrogen phosphate (ADP) is an inorganic material widely used as second, third and fourth harmonic generator for Nd: YAG and Nd: YLF lasers. Studies of ADP crystals are gaining more interest because of their unique nonlinear optical, dielectric, piezoelectric and antiferroelectric properties [1–3]. Many researchers have investigated pure and doped ADP crystals to study the enhancement in electrical, nonlinear and ferroelectric properties. The improved optical transmission and electrical conductivity of ADP doped with L-alanine crystals have been reported by Akhtar and Podder [4]. An effect of L-lysine on growth and various properties of ADP has been reported by Rajesh et al. [5]. An effect of L-arginine and glycine on growth and various properties of ADP has been reported by Pattanaboonmee et al. [6]. Structural, optical, dielectric and mechanical study of L-proline doped ADP has been reported by Hasmuddin et al. [7]. Brahim and Bulou [8] have reported growth and detailed analysis of MAS NMR, FT-IR and Raman spectroscopic studies of different mole% LC doped ADP crystal and also reported its tetragonal structure by powder XRD. However, to the best of our knowledge no report is available in the literature on the linear–nonlinear optical, electrical, mechanical and thermal properties of LC doped ADP crystal. Therefore, in the present communication we have reported the effect of LC on linear–nonlinear optical, electrical, mechanical and thermal properties of ADP crystal. These properties are very crucial for any material to be used for NLO applications.

2. Experimental procedure

The amino acid LC was added in three different mole% in the super saturated solution of AR grade ADP. The homogeneous solutions were prepared by constant stirring for 6 h. The solutions were then filtered and kept for slow evaporation at room temperature. The good quality transparent seed crystals were harvested within 7–8 days. The salts of these three mole% LC doped ADP crystals were subjected to SHG test at Indian Institute of Science Bangalore and highest SHG efficiency was observed with 0.08 mole% LC doped ADP crystal powder; hence the bulk crystal of the same was grown by the slow evaporation technique (Fig. 1).

3. Results and discussion

3.1. FT-IR spectral analysis

The FT-IR spectrum of LC doped ADP crystal was recorded using the Bruker α-ATR spectrophotometer in the range of 600–4000 cm^{-1} to confirm the incorporation of LC in ADP crystal. The recorded transmittance FT-IR spectrum of grown crystal is depicted in Fig. 2. In the spectrum the broad band around 3610–2530 cm^{-1} was due to the O–H vibrations of P–O–H group and N–H vibrations of NH_4. The band at 2302 cm^{-1} was observed due to hydrogen bond.

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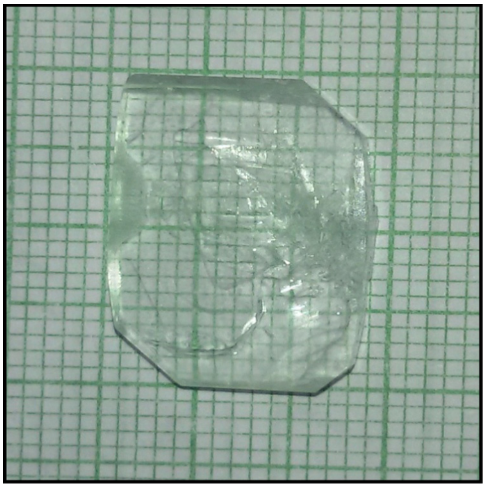

Fig. 1. Photograph of LC doped ADP crystal.

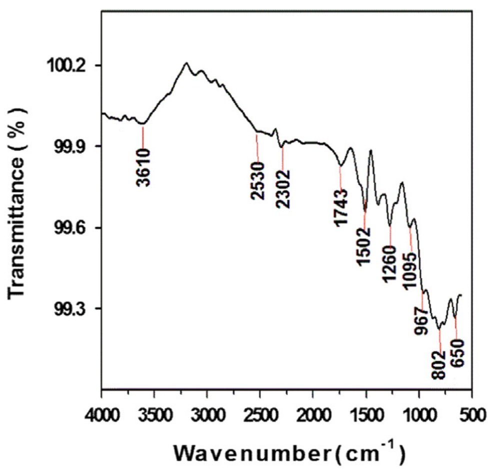

Fig. 2. FT-IR spectrum of LC doped ADP crystal.

The peak at 1502 cm^{-1} was due to N–H vibrations. The strong band at 1260 cm^{-1} was observed due to the combination of the asymmetric stretching vibration of PO_4 with lattice. The peaks at 1095 cm^{-1} and 967 cm^{-1} represent P–O–H vibrations. These peaks are same as those of pure ADP with slight shift in wave numbers from lower to higher, due to the presence of LC in ADP [4,7]. The additional peaks at 1743 cm^{-1} were observed due to C=O stretching and the peak at 650 cm^{-1} was observed due to C–S stretching [8].

3.2. SHG efficiency

The NLO properties of LC doped ADP crystal were studied using a classical Kurtz and Perry powder technique [9] using Q-switched Nd: YAG laser delivering input beam energy of 2.8 mJ/pulse at the wavelength of 1064 nm with repetition rate of 10 Hz and pulse width of 8 ns. The finely powdered samples of 0.08, 0.16, and 0.24 mole% LC doped ADP crystals were tightly packed in the microcapillary tube of uniform bore and illuminated with the polarized beam of laser. The bright green light shown at the output of the subjected samples confirmed the prominent generation of second harmonic signals. The corresponding output voltages recorded for KDP and 0.08 mole% LC doped ADP crystals are 15.2 mV and 31.2 mV. The rise in SHG efficiency of LC doped ADP crystal is observed due to high mobility of charge carriers through π-bonding network of dopant LC. Thus, SHG efficiency of LC doped ADP crystal is nearly double that of KDP suggesting its prominence for NLO application [10].

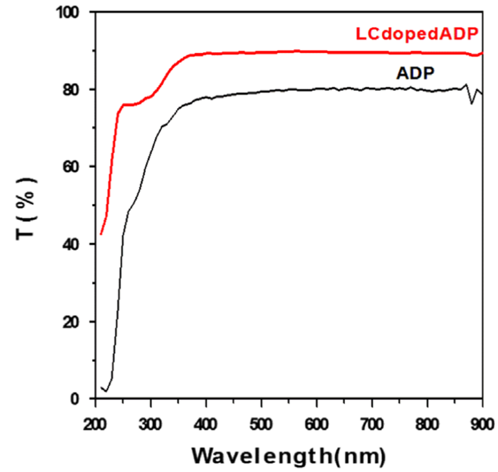

Fig. 3. UV–vis transmittance spectrum.

3.3. UV–visible studies

The UV–visible study of LC doped ADP crystal was undertaken in the range of 200–900 nm using a Shimadzu UV-2450 spectrophotometer. The transmittance spectrum of grown crystal shown in Fig. 3 reveals the large transmission range of doped ADP crystal which is extending to the UV region. This might be due to prominent n to π^* transitions offered by nitrogen and hydrogen bonds in organic compound LC [11]. The transparency of LC doped ADP crystal is more than 89% in entire visible region which confirms its suitability for SHG transmission devices [12]. The dependence of absorption coefficient on incident photon energy helps to evaluate the band gap of material using the relation $(\alpha h\nu)^2 = A(h\nu - E_g)$ [12]. The optical band gap of pure and LC doped ADP crystal was determined using Tauc's extrapolation method as depicted in Fig. 4. The optical band gap of LC doped ADP is found to be 5.35 eV which is greater than pure ADP. The wide optical band gap of LC doped ADP crystal suggests its effective utility for optoelectronic applications [12–14].

3.4. Z-scan studies

The optically transparent LC doped ADP crystal was subjected to *Z*-scan measurement using He–Ne laser operating at 632.8 nm. The polarized Gaussian beam was focused on the crystal through the lens of focal length 12 cm and it was gradually translated along the *Z*-direction pre and post the focus ($Z=0$). The refraction nonlinearity originated due to localized absorption of repetitive incident optical field was recorded using the closed aperture of an optical detector placed at a far field [15]. The peak to valley transmission difference can be evaluated using following equation [15]:

$$\Delta T_{p-v} = 0.406(1-S)^{0.25}|\Delta\phi| \quad (1)$$

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 nonlinear refractive index was calculated as

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

where $K = 2\pi/\lambda$, I_0 is the intensity of the laser beam at the focus $Z=0$, $L_{eff} = [1 - \exp(-\alpha L)]/\alpha$ is the effective thickness of the sample depending on linear absorption coefficient (α) and L is thickness of the sample.

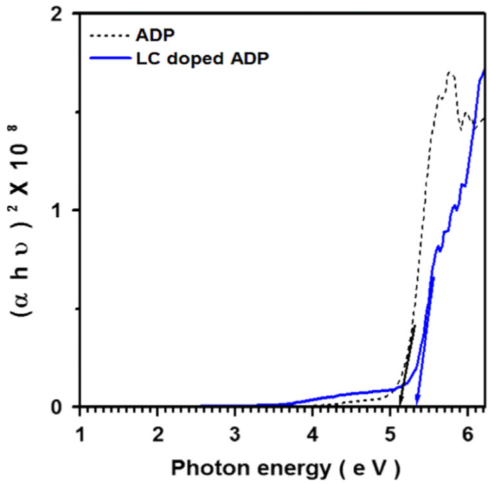

Fig. 4. Tauc's plot.

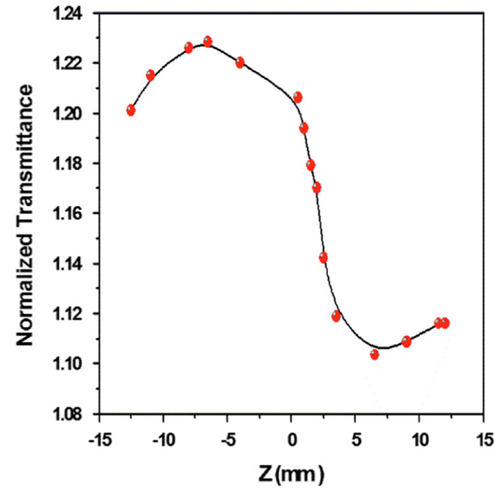

Fig. 5. Closed aperture Z-scan curve.

From open aperture Z-scan data, the nonlinear absorption coefficient β is estimated using following equation:

$$\beta = \frac{2\sqrt{2}\Delta T}{I_0 L_{eff}} \tag{3}$$

where ΔT is the one valley value detected in open aperture Z-scan curve. The third order nonlinear susceptibility of doped ADP crystal was calculated using the relations depicted below

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

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

$$\chi^3 = \sqrt{(\mathrm{Re}\chi^3)^2 + (\mathrm{Im}\chi^3)^2} \tag{6}$$

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. Fig. 5 depicts the peak to valley phase distortion exhibited by grown crystal indicating the self defocusing nature or negative index of refraction. The negative index of refraction of LC doped ADP crystal makes it prominent material for protection optical night vision sensor devices [16]. The nonlinear refractive index is found to be -5.63×10^{-12} cm²/W. The open aperture transmittance data shown in Fig. 6 confirmed the reverse saturable absorption phenomenon by the doped ADP crystal which originates as a result of absorption of incident photon due to excited states [17]. The third order nonlinear susceptibility of grown crystal is found to be 1.45×10^{-5} esu which is notably higher than KDP crystal [18]. The enhanced delocalization of conjugated π electron is the principal factor responsible for higher nonlinear behavior [19]. The optical details of the Z-scan setup and measured nonlinear optical parameters of the grown crystal are systematically arranged in Table 1. The figure of merit (FOM) was evaluated using the relation $(\beta\lambda/n_2)$. The FOM value of grown crystal is found to be 59.8 indicating its suitability for photonics applications [20]. The promising third order NLO properties of LC doped ADP crystals suggest its suitability for optical limiting and photonics devices [13,20].

3.5. Dielectric studies

The temperature dependent dielectric studies of LC doped ADP crystal were undertaken using the HIOKI 3250 instrument using 1.87 mm crystal sample. The crystal surface of sample was smoothly silver pasted and placed between the copper electrodes for electrical contacts. The dielectric study was carried at different temperatures ranging from 40 to 80 °C with interval of 20 °C. The

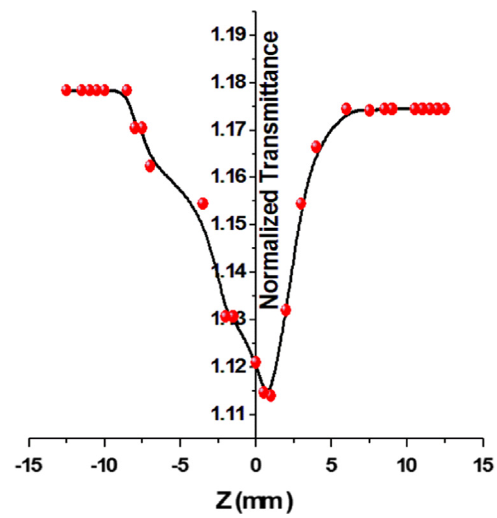

Fig. 6. Open aperture Z-scan curve.

Table 1
Optical detail of Z-scan setup and measured parameters.

Laser beam wavelength (λ) (nm)	632.8
Lens focal length (f) (cm)	12
Optical path distance (Z) (cm)	115
Spot-size diameter in front of the aperture (ω_a) (cm)	1
Aperture radius (r_a) (mm)	4
Incident intensity at the focus (Z=0) (MW/cm²)	3.13
Effective thickness (L_{eff}) (mm)	1.45
Nonlinear refractive index (n_2) (cm²/W)	-5.63×10^{-12}
Nonlinear absorption coefficient (β) (cm/W)	5.32×10^{-6}
Third-order nonlinear susceptibility (χ^3) (esu)	1.45×10^{-5}

dielectric constant is calculated using the relation: $\varepsilon = Cd/\varepsilon_0 A$ where C is the capacitance, d is the thickness, and A is the area of the sample. Fig. 7 shows the variation of dielectric constant with frequency (F); it could be seen that ε_r decreases with increasing frequency, and increases with rise in temperature range taken for present investigation. The dielectric constant of a material is due to the contribution of electronic, ionic, dipolar and space charge polarization, which depends on the frequencies of applied field. The variation of dielectric loss as a function of frequency and temperature is shown in Fig. 8 which exhibits the same behavior as that of dielectric constant. The low value of dielectric loss indicates that grown crystal possesses the good quality and lesser

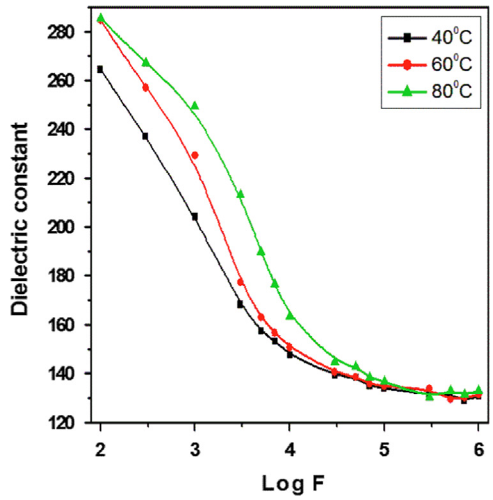

Fig. 7. Dielectric constant vs. log F.

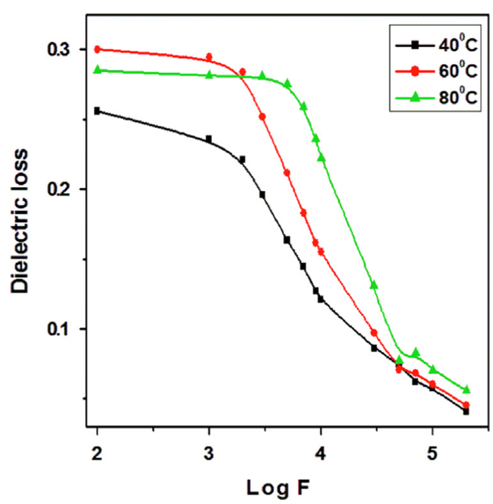

Fig. 8. Dielectric loss vs. log F.

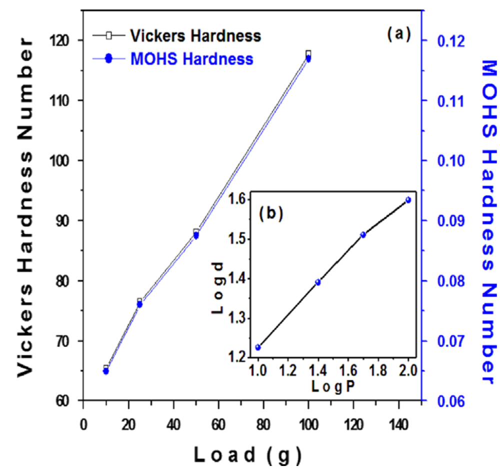

Fig. 9. (a) Hardness number vs. load (P) and (b) log P vs. log d.

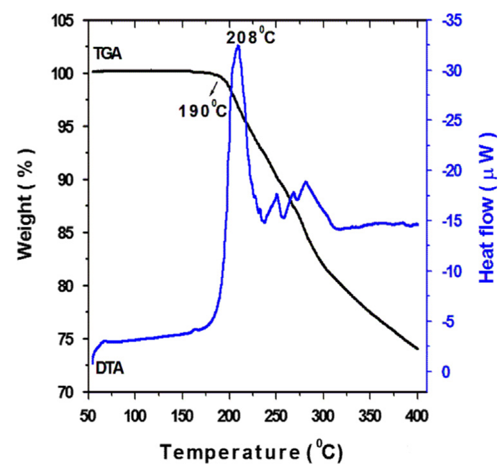

Fig. 10. TG–DTA curve of LC doped ADP.

number of electrically active defects. These parameters have the vital importance for microelectronics and NLO applications [21].

3.6. Micro-hardness studies

To find surface hardness of the grown LC doped ADP crystal, microhardness was measured from 10 to 100 g load for indention time of 10 s using Vicker's microhardness tester. Vicker's hardness number (H_v) was calculated using the standard formula: $H_v = 1.8544p/d^2$, where p is the applied load in kg, d is the mean diagonal length in mm and H_v is in kg mm^{-2}. The variation of Vickers and MOHS hardness value with increasing load displayed in Fig. 9(a) shows that the hardness increases with increase of load [22]. The hardness of doped ADP crystal is higher than pure ADP [5]. Meyer's index number was calculated from Meyer's law, which relates the load and indention diagonal length as the $P = k \times d^n$, where k is the material constant and n is Meyer's index [23]. In order to find the value of 'n' a graph of log P against log d is plotted in Fig. 9(b), which gives a straight line. From the slope of line Meyer's index number 'n' was calculated to be 2.55. According to Onitsch criteria the value of 'n' lies between 1 and 1.6 for hard materials and is greater than 1.6 for soft materials [23]. The 'n' value calculated in the present studies is > 1.6 suggesting that the grown LC doped ADP crystal belongs to category of soft material.

3.7. Thermal studies

The thermal behavior of LC doped ADP crystal was investigated using the PerkinElmer Diamond thermal analyzer in a homogeneous nitrogen atmosphere at a heating rate of 20 °C/min. The simultaneous TG/DTA thermogram of LC doped ADP crystal is shown in Fig. 10. The DTA curve shows an endothermic peak at 208 °C at the same time weight loss started at 190 °C. It is observed from thermogram that the further increase in temperature evidences the gradual decomposition of the compound. The melting point of LC doped ADP crystal is exclusively higher than L-lysine doped ADP crystal [5].

4. Conclusion

The amino acid LC doped ADP was grown by the slow evaporation technique. The dopant LC promoted the transmittance of ADP up to 89% and optical band gap up to 5.35 eV; this indicates that LC doped ADP crystal is suitable for optical applications. The thermal study revealed that the grown crystal can be exploited to any application below 208 °C. The dielectric study revealed that LC doping reduces the dielectric constant and dielectric loss, which confirms its suitability for microelectronics application. Microhardness analysis reveals that grown crystal belongs to soft material category. The SHG efficiency of LC doped ADP is found to be two times more than KDP. The nonlinear refractive index, absorption coefficient and third order susceptibility are found to be -5.63×10^{-12} cm^2/W, 5.32×10^{-6} cm/W, and 1.45×10^{-5} esu respectively. All above investigations suggest the prominence of grown crystal for distinct NLO applications.

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References

[1] Dhumane NR, Hussaini SS, Dongre VG, Shirsat MD. Influence of glycine on the nonlinear optical (NLO) properties of zinc (tris) thiourea sulfate (ZTS) single crystal. Opt Mater 2008;31:328–32.
[2] Dhanaraj PV, Bhagavannarayana G, Rajesh NP. Effect of amino acid additives on crystal growth parameters and properties of ammonium dihydrogen orthophosphate crystals. Mater Chem Phys 2008;112:490–5.
[3] Rajesh P, Ramasamy P. Growth of DL-malic acid-doped ammonium dihydrogen phosphate crystal and its characterization. J Cryst Growth 2009;311:3491–7.
[4] Akhtar Ferdousi, Podder Jiban. Structural, optical, electrical and thermal characterizations of pure and L-alanine doped ammonium dihydrogen phosphate crystals. J Cryst Process Technol 2011;1:18–25.
[5] Rajesh P, Ramasamy P, Mahadevan CK. Effect of L-lysine monohydrochloride dihydrate on the growth and properties of ammonium dihydrogen orthophosphate single crystals. J Cryst Growth 2009;311:1156–60.
[6] Pattanaboonmee N, Ramasamy P, Yimnirun R, Manyum P. A comparative study on pure, L-arginine and glycine doped ammonium dihydrogen orthophosphate single crystals grown by slow solvent evaporation and temperature-gradient method. J Cryst Growth 2011;314:196–201.
[7] Hasmuddin Mohd, Singh Preeti, Shkir Mohd, Abdullah MM, Vijayan N, Bhagavannarayana G, et al. Structural, spectroscopic, optical, dielectric and mechanical study of pure and L-proline doped ammonium dihydrogen phosphate single crystals. Spectrochim Acta A 2014;123:376–84.
[8] Brahim FB, Bulou A. Growth and spectroscopy studies of ADP single crystals with L-glutamine and L-cysteine amino acids. Vib Spectrosc 2013;65:176–85.
[9] Kurtz SK, Perry TT. A powder technique for the evaluation of nonlinear optical materials. J Appl Phys 1968;39:3798 (-3813).
[10] Parthasarathy M, Anantharaja M, Gopalakrishnan R. Growth and characterization of large single crystals of L-serine methyl ester hydrochloride. J Cryst Growth 2012;340:118–22.
[11] Subhashini V, Ponnusamy S, Muthamizhchelvan C. Synthesis, growth, spectral, thermal, mechanical and optical properties of piperazinium (meso) tartrate crystal: a third order nonlinear optical material. J Cryst Growth 2013;363:211–9.
[12] Rajalakshmi M, Indrajith R, Ramasamy P, Gopalkrishnan R. Synthesis, growth and characterization of 1H-benzimidazolium hydrogen L-tartrate dihydrate single crystals. Mol Cryst Liq Cryst 2011;548:126–41.
[13] Mohd Anis, Shirsat MD, Muley G, Hussaini SS. Influence of formic acid on electrical, linear and nonlinear optical properties of potassium dihydrogen phosphate (KDP) crystals. Physica B 2014;449:61–6.
[14] Shaikh RN, Mohd. Anis, Shirsat MD, Hussaini SS. Investigation on the linear and nonlinear optical properties of L-lysine doped ammonium dihydrogen phosphate crystal for NLO applications. J Appl Phys 2014;6:42–6.
[15] Bahae MS, Said AA, Wei TH, Hagan DJ, Van Stryland EW. Sensitive measurement of optical nonlinearities using a single beam. IEEE J Quantum Electron 1990;26:760–9.
[16] Dhanaraj PV, Rajesh NP. Investigations on crystal growth, structural, optical, dielectric, mechanical and thermal properties of a novel optical crystal: nicotinium nitrate monohydrate. J Cryst Growth 2011;318:974–8.
[17] Sajan D, Vijayan N, Safakath K, Reji Philip, Hubert Joe I. Intramolecular charge transfer and *Z*-scan studies of semiorganic nonlinear optical material sodium acid phthalate hemihydrate: a vibrational spectroscopic study. J Phys Chem A 2011;115:8216–26.
[18] Ganeev RA, Kulagin IA, Ryasnyansky AI, Tugushev RI, Usmanov T. Characterization of nonlinear optical parameters of KDP, $LiNbO_3$ and BBO crystals. Opt Commun 2004;229:403–12.
[19] G´omez SL, Cuppo FLS, Figueiredo Neto AM. Nonlinear optical properties of liquid crystals probed by *Z*-scan technique. Braz J Phys 2003;33:813–20.
[20] Anusha PT, Silviya Reeta P, Giribabu L, Tewari SP, Venugopal Rao S. Picosecond nonlinear optical studies of unsymmetrical alkyl and alkoxy phthalocyanine. Mater Lett 2010;64:1915–7.
[21] Kannan V, Thirupugalmani K, Shanmugam G, Brahadeeswaran S. Synthesis, growth, thermal, optical, mechanical and dielectric studies of N-succinopyridine. J Therm Anal Calorim 2013. http://dx.doi.org/10.1007/s10973-013-3269-y.
[22] Gilman John J. Chemistry and physics of molecular hardness. Hoboken, NJ: John Wiley & Sons, Inc.; 2009.
[23] Kalainathan S, Jagannathan K. Mechanical and surface analysis of stilbazolium tosylate derivative crystals. J Cryst Growth 2008;310:2043–9.