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Investigations on the supramolecular assemblies of pyridine based organic crystals for nonlinear optical applications

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Present work aims at the crystal growth and characterization of 2-amino 4, 6 dimethoxypyrimidine p-toluenesulfonic acid monohydrate (2ADPTS), 2, 6 diaminopyridiniumtosylate (2,6DPT), isonicotinamidium picrate (ISPA) and 2-aminopyridinium diphenylacetatediphenylacetic acid (2APD) by slow evaporation solution technique (SEST). The essential properties, such as structural, linear and nonlinear optical, thermal and laser damage threshold of the grown crystals have been investigated.

Keywords: Crystal, NLO, HRXRD, FTIR

1. Introduction

In the modern world, crystal growth is a huge field of activity encompassing theoretical and experimental research, production of crystals and device fabrication. The understanding of crystal growth processes and the phenomena associated with it is being increased in the study of scientific and medical areas [1]. This became true after the discovery of novel materials which bridge the gap between technology and human life. Single crystals form the foundation of modern technology. Silicon is, perhaps, the most obvious example, but many other types of crystals are required for lasers, optical components for spectroscopy and communications, oscillators, light-emitting diodes etc. A simple fact is that, only with the support of crystal growers, there would be electronic industry, fiber-optic communications, very little modern optical equipment and some very important conventional production engineering. Pyridine is a good hydrogen bond acceptor and a strong organic base [2]. It is capable of forming ionic co-crystals by proton transfer through hydrogen bonding interactions with many of the acids. Several nonlinear optical complexes formed from pyridine derivatives have been crystallized and their structure has been reported for the first time in the literature. In such a way, the present work deals with the growth and physico-chemical properties of 2-amino 4, 6 dimethoxypyrimidine p-toluenesulfonic acid monohydrate (2ADPTS), 2, 6 diaminopyridiniumtosylate (2,6DPT), isonicotinamidium picrate (ISPA) and 2-aminopyridinium diphenylacetatediphenylacetic acid (2APD) organic bulk single crystals and their characterization studies.

2. Material synthesis and crystal growth

All the four crystals namely 2ADPTS, 2,6DPT, ISPA and 2APD were grown by adopting slow evaporation solution growth technique. The solubility of the grown crystals was performed using a constant temperature bath (CTB) with temperature accuracy of ± 0.01°C. The solubility of the grown 2ADPTS, 2,6DPT, ISPA and 2APD were found to be 20 g/100 mL, 16.9 g/100 mL, 2.9 g/100 mL and 15.2 g/100 mL respectively. The solubility of the grown crystals is shown in Figure 1. The 2ADPTS crystal was grown at 35˚C whereas 2,6DPT and ISPA crystalswere grown at 40˚C. The 2APD crystal with a moderate solubility was grown at 45˚C. The grown crystals are shown in Figure 2.

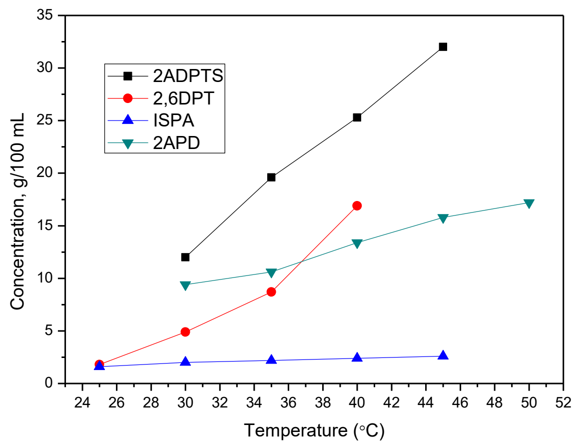

Figure 1. Solubility of the grown crystals

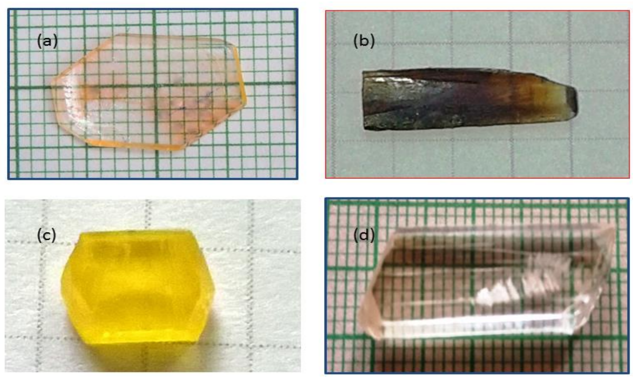

Figure 2. (a) As grown 2ADPTS crystal, (b) As grown 2,6DPT crystal, (c) As grown ISPA crystal, (d) As grown 2APD crystal

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3. Results and discussion

3.1 Single crystal X-ray diffraction study

The single crystal X-ray diffraction study reveals that the 2ADPTS crystal crystallizes in triclinic crystal system with space group $P\bar{1}$.All the other three crystals, such as 2,6DPT, ISPA and 2APD crystallizes in the monoclinic crystal system with space group $P2_1/c$, $P2_1/n$ and $P2_1$ respectively. All the crystals were structure solved and reported in Cambridge crystallographic data collection center with CCDC numbers 991931, 1010923, 1058823 and 1444071 respectively. The ORTEP and packing diagram of the grown crystals are shown in Figure 3.

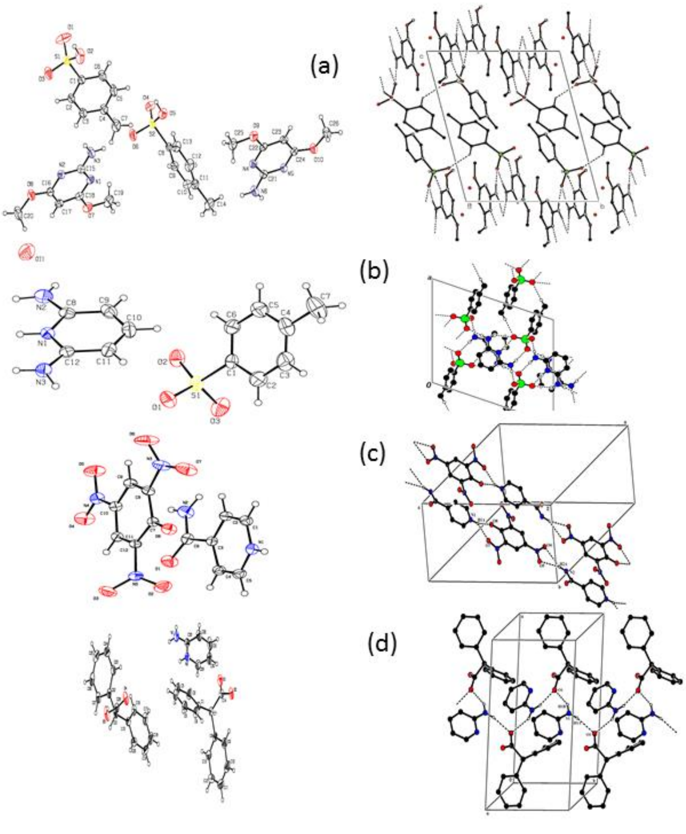

Figure 3. ORTEP and packing of (a) 2ADPTS (b) 2,6DPT (c) ISPA and (d) 2APD

3.2 Optical transmittance study

UV-vis-NIR spectral study was carried out in the range 190–900 nm by labIndia 3032 spectrophotometer. The 2ADPTS crystal has sufficient transmittance in the visible and IR regions and has good transparency of 50% with lower cut-off wavelength of 296 nm, whereas 2,6DPT, ISPA and 2APD crystals have sufficient transmittance around 40%, 70% and 67% with lower cut-off wavelength being 380 nm, 469 nm and 349 nm respectively as shown in Figure 4. The band gap of the crystals estimated by extrapolation of the linear part to the onset of the energy axis of the graph, as shown in Figure 5, is 4.12 eV, 3.14 eV, 2.69 eV and 3.55 eV respectively.

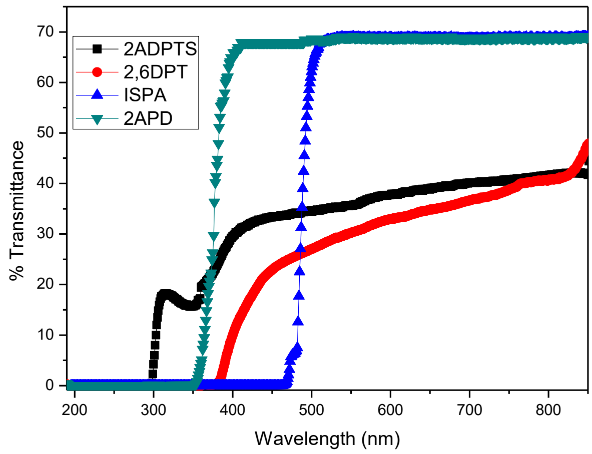

Figure 4. Optical transmittance spectra of the grown crystals

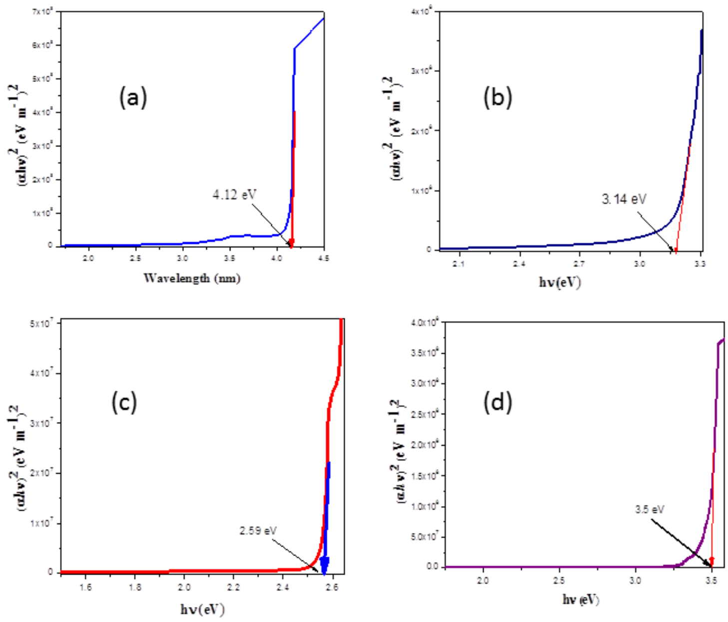

Figure 5. Tauc's plot of a) 2ADPTS b) 2,6DPT c) ISPA d) 2APD

3.3 High resolution X-ray diffraction study

The crystalline perfection of the grown single crystal was characterized by HRXRD technique employing a multicrystal X-ray diffractometer developed at NPL, New Delhi, India [3]. The FWHM (full width at half maximum) of the grown 2ADPTS and 2,6DPT are found to be 115 arc s and 58 arc s respectively, as shown in Figure 6. It is observed that thediffraction curve contains a single peak which indicates that the specimen is free from structural grain boundaries.

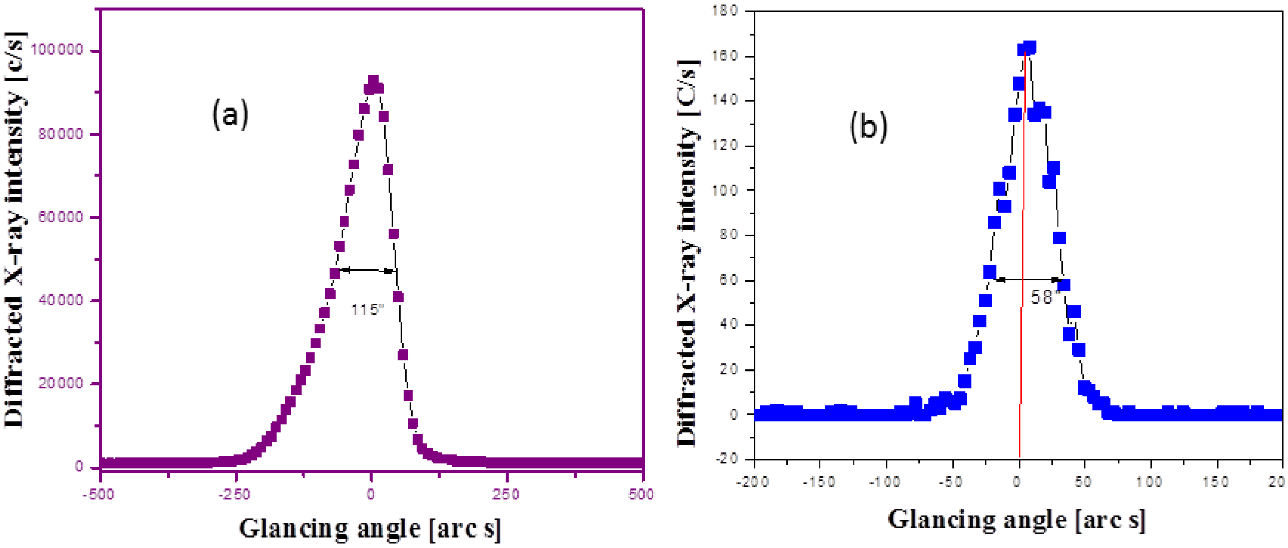

Figure 6. HRXRD curves of (a) 2ADPTS and (b) 2,6DPT crystals

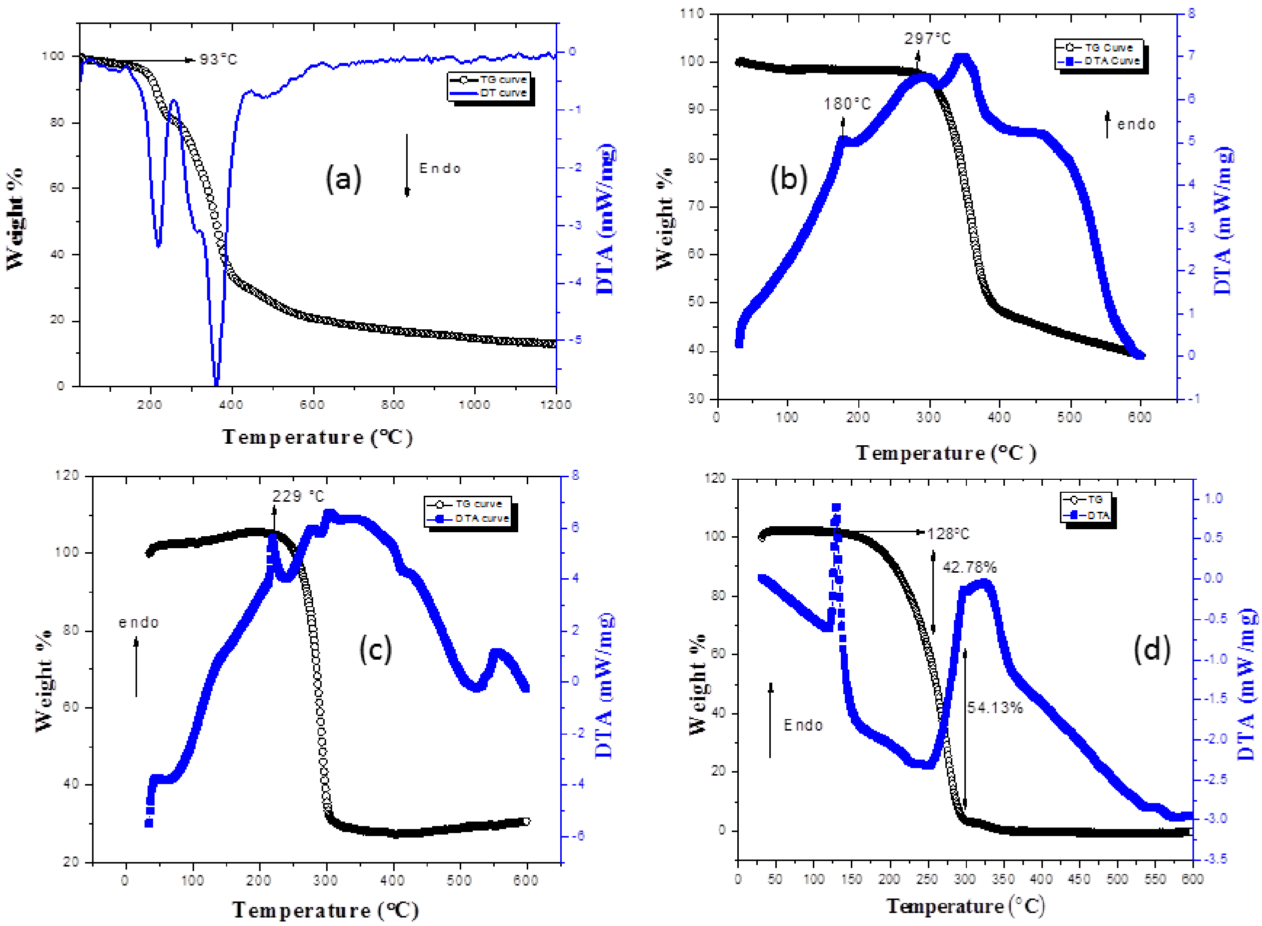

Figure 7. TG-DTA curves of (a) 2ADPTS (b) 2,6DPT (c) ISPA and (d) 2APD

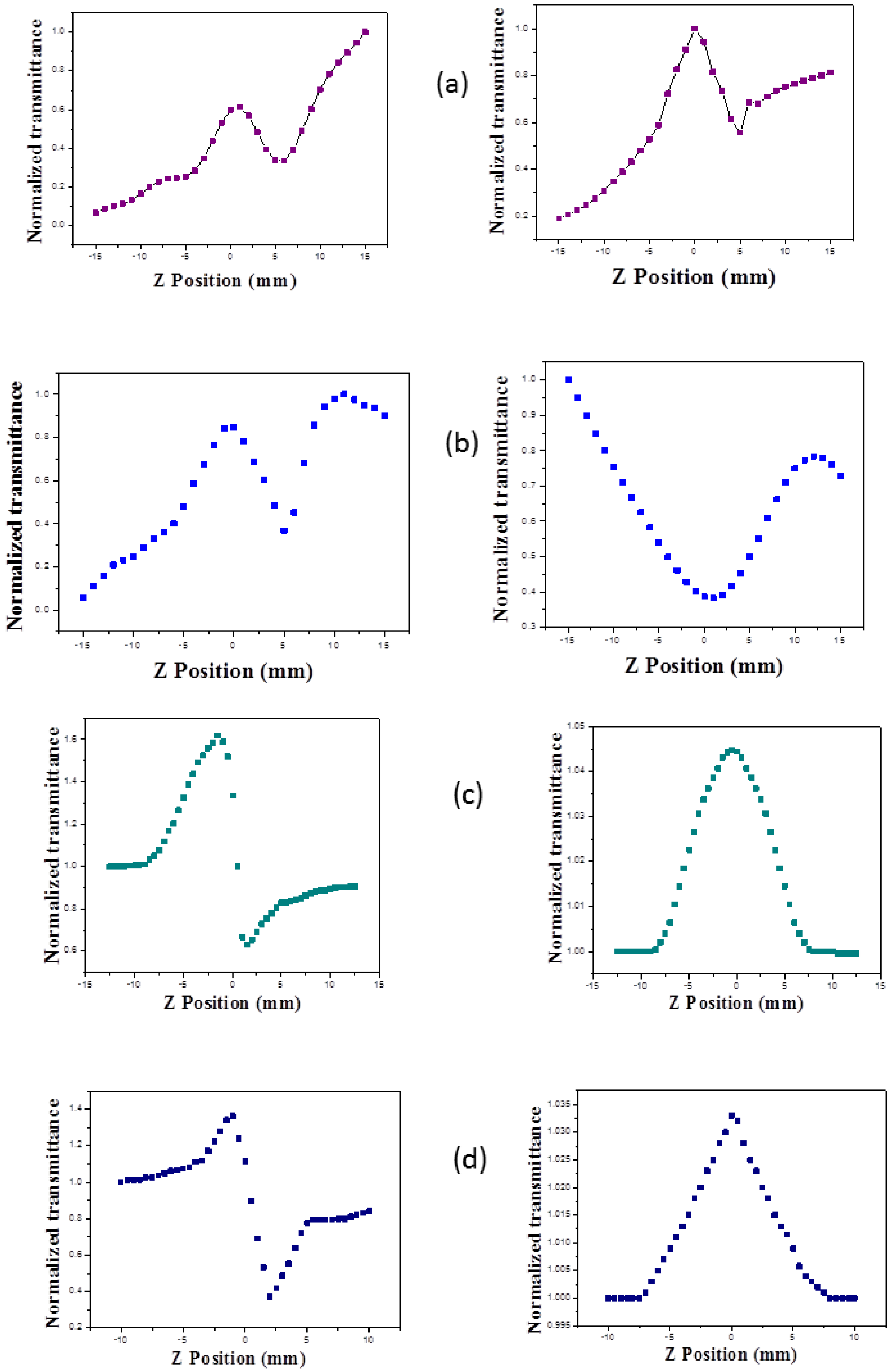

Figure 8. Open and closed aperture curves of (a) 2ADPTS (b) 2,6DPT (c) ISPA and (d) 2APD crystals

3.4 **Thermal analysis**

The thermal stability of the grown crystals was studied by thermogravimetric (TG) and differential thermal analysis (DTA). From the TG curve, it is evident that the grown crystal, such as 2ADPTS, 2,6DPT, ISPA and 2APD are thermally stable up to 93°C, 180°C, 229°C and 128°C respectively. The endotherm in the DTA curve found associated with the weight loss confirms the absorption of energy for breaking of bonds during decomposition [4]. The recorded TG-DTA curves are shown in Figure 7.

3.4 Laser damage threshold study

Laser damage threshold of the grown crystals was determined using an Nd:YAG laser. The laser damage threshold depends on a great number of laser parameters, such as wavelength, energy, pulse duration, longitudinal and transverse mode structure, beam size, location of beam etc., [5]. Three methods are reported in literature to measure LDT values. (1) One-shot per site (referred as ''1 on 1'' method): here one shot is made per site and the next shot after increasing the intensity is made at a fresh site. This process is repeated till the damage occurs; (2) N shots per site (referred as ''N or S on 1'' method): here a single site is targeted by a fixed 'N' number of shots of same intensity. If in case no damage occurs, the procedure mentioned above is repeated at another site with increase of intensity. This is continued till the damage occurs and (3) multiple shots per site with ramped increase of intensity of every shot until the damage occurs to the spot. This is referred as ''R on 1'' method [6]. In the present work 1 on 1 method was employed to determine the laser damage threshold of the grown crystals. The surface damage threshold of the crystal was calculated using the expression:

$$\text{Power density, } P_d = \frac{E}{\tau \pi r^2}$$

where E is the input energy (mJ), τ is the pulse width (ns) and r is the radius of the spot (mm). The measured multiple shot (10 pulses) laser damage threshold value of 2ADPTS, 2,6DPT, ISPA and 2APD are found to be 2.6 GW cm^{-2}, 0.25 GW cm^{-2}, 0.23 GW cm^{-2}, and 0.97 GW cm^{-2}respectively for 1064 nm wavelength of Nd:YAG laser radiation.

3.5 Nonlinear optical study

The Z-scan technique is an increasingly popular method for the measurement of optical nonlinearities of materials, not only because it has the advantages of simplicity and high sensitivity, but also it can simultaneously measure the magnitude and sign of the nonlinear refractive index (n_2) and the nonlinear absorption coefficient (β) of the samples [7]. The calculated third order nonlinear optical parameters such as nonlinear refractive index (n_2), nonlinear absorption coefficient (β) and third order nonlinear optical susceptibility ($\chi^{(3)}$) of the grown 2ADPTS, 2,6DPT, ISPA and 2APD are tabulated and shown in Table 1. The open and closed aperture curves of the grown crystals are shown in Figure 8.

Table 1 Nonlinear optical parameters of the grown crystals

Name of the crystal	β (cm/W)	χ^3(esu)
2ADPTS	0.311×10^{-2}	3.143×10^{-4}
2,6DPT	0.063×10^{-2}	4.256×10^{-3}
ISPA	0.43×10^{-4}	4.48×10^{-6}
2APD	0.03×10^{-4}	5.10×10^{-6}

β – Nonlinear absorption coefficient
χ^3 – Third order nonlinear optical susceptibility

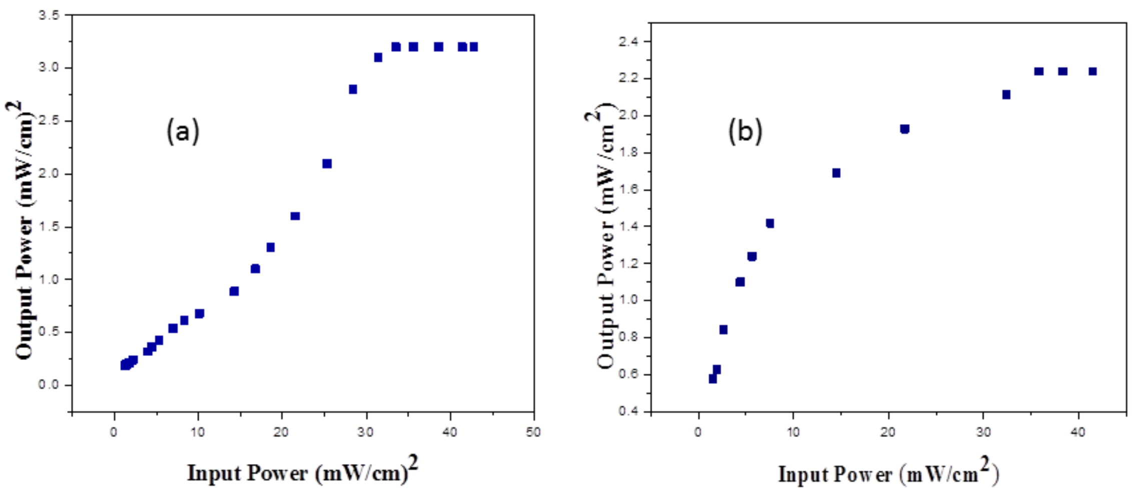

Figure 9. Optical limiting curves of (a) ISPA and (b) 2APD crystals

3.6 Optical limiting study

Optical limiters are devices designed to have high transmittance for low level inputs while blocking the transmittance for high intensity laser beams. Since the development of the first lasers in the late 1960's passive optical limiters have been built and tested to protect optical sensors against laser-induced damage [8]. The optical limiting behavior of the grown ISPA and 2APD crystal was tested by varying the input laser power systematically and the corresponding output power values were measured by the photo detector. As can be seen from Figure 9, the output power of ISPA and 2APD crystal increases with the increase of the input power at lower power regions and then found to saturate from the threshold of 3.25 mW/cm^2, 2.24 mW/cm^2 and amplitude of 32 mW/cm^2, 36 mW/cm^2.

4. Conclusions

In summary, crystal growth and characterization of 2-amino 4, 6 dimethoxypyrimidine p-toluenesulfonic acid monohydrate (2ADPTS), 2, 6 diaminopyridiniumtosylate (2,6DPT), isonicotinamidium picrate (ISPA) and 2-aminopyridinium diphenylacetatediphenylacetic acid (2APD) have been grown by slow evaporation solution technique (SEST). The essential properties, such as structural, linear and nonlinear optical, thermal and laser damage threshold of the grown crystals have been found and reported. The grown crystals, based on their properties, are found to be good candidates for nonlinear optical applications.

References

1) Chemla D. S. andZyss. J (1987), Nonlinear Optical Properties of Organic Molecules and Crystals, Academic Press, New York.

2) Dryburgh P.M (1986), 'Sixth International summer school on crystal growth', Edinburgh.

3) Bhagavannarayana G., Rajesh P., Ramasamy P., (2010), 'Interesting growth features in potassium dihydrogen phosphate: unravelling the origin and dynamics of point defects in single crystals', J. Appl. Cryst., Vol. 43, pp. 1372–1376.

4) Jauhar RO. MU.,Viswanathan. V, Vivek. P, Vinitha. G, Velmurugan. D and Murugakoothan.P (2016), RSC Advances, 6 57977.

5) Bhar G.C., Chaudhury A.K., Kumbhakar P., (2000) 'Study of laser induced damage threshold and effect of inclusions in some nonlinear crystals', Appl. Surf. Sci., Vol. 161, pp. 155–62.

6) Sharma S.K., Sunil Verma, Yeshpal Singh, Bartwal K.S., Tiwari M.K., Lodha G.S., Bhagavannarayana G., (2015), 'Investigations of structural defects, crystalline perfection, metallic impurity concentration and optical quality of flat-top KDP crystal', Opt. Mater., Vol. 46, pp. 329-338.

7) Sheik-Bahae M., Said A.A., Wei T., Hagan D.J., Van Stryland E.W., (1990) 'Sensitive measurement of optical nonlinearities using a single beam', IEEE J. Quantum Electron, Vol. 26, pp. 760-769.

8) Fryad Z. Henari and Patil P.S., (2014), 'Nonlinear Optical Properties and Optical Limiting Measurements of {(1Z)-[4 (Dimethylamino)Phenyl]Methylene} 4-Nitrobenzocarboxy Hydrazone Monohydrate under CW Laser Regime', Optics and Photonics Journal, Vol. 4, pp. 182-188.