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The non-linear optical crystal growth and characterization of piperizantum p- aminobentzone

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Abstract

The nonlinear optical properties of piperizanium p – aminobenzoate (PZPAB) crystal were successfully grown with the help of temperature gradient (Slow evaporation) method. The good quality of PZPAB single crystal is formed. The PZPAB is characterized with the help of X-ray diffraction (XRD), Fourier transform infrared (FTIR) measurement, photoluminescence (PL), Raman spectroscopy, ultra violet visible spectroscopy (UV) and finally etching analysis was done.

Keywords: Piperizanium p – aminobenzoate; nonlinear optical crystal; slow evaporation method.

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1. Introduction

A material that has good crystalline nature is also having good optical and electrical properties [1-3]. Many organic and inorganic crystal materials had high polarization ability and are good candidates for nonlinear optical (NLO) studies [4]. However, the net polarization depends on the material symmetry properties, with respect to the impinging fields. So far, there are many organic crystals which is used for NLO yet, piperizanium p- aminobenzoate having the adorable nature of nonlinear properties. In the present article, gives the advancement of new NLO material (piperizanium p- aminobenzoate); which is being characterized with the help of XRD, FTIR, UV, Raman and PL.

2. Materials and Methods

Piperazinium p-aminobenzoate crystal was prepared in the room temperature by slow evaporation growth method [5] by using as a methanol solvent. The precursor's materials of Piperazine (98%) and p-aminobenzoic acid (99%) were taken in the equimolar ratio of 1:1 for the synthesis process is shown in figure 1. The p-Aminobenzoic acid was first dissolved in the solvent of methonal, after

complete dissolved acid material and then the base compound of Piperazine was added little by little with the acid solution. The solution is allowed to get a homogenous mixture by continuously stirring for 8 hours using the temperature control magnetic stirrer in the room temperature circumstances [5]. After attaining the homogenous saturated state the solution was filtered using the whatman filter paper which is having the fine holes in the range of 110 μm and the filtered solution was covered with the perforated sheet having the fine holes for the evaporation and it was kept at the room temperature without disturbance. After 2 successive recrystallization process the good quality PZPAB crystal was harvested with in the span of 60 days. The figure 2 shows the crystal of PZPAB.

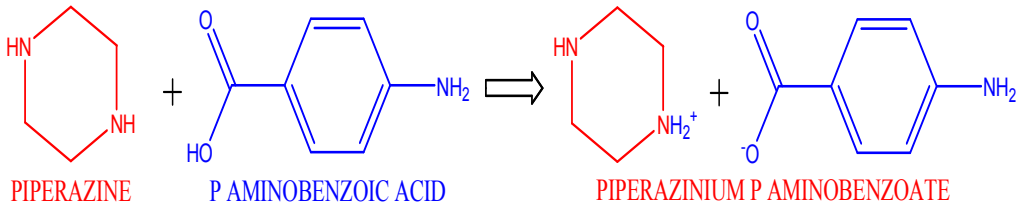

Fig. 1: Synthesis scheme of Piperazinium P-Aminobenzoate.

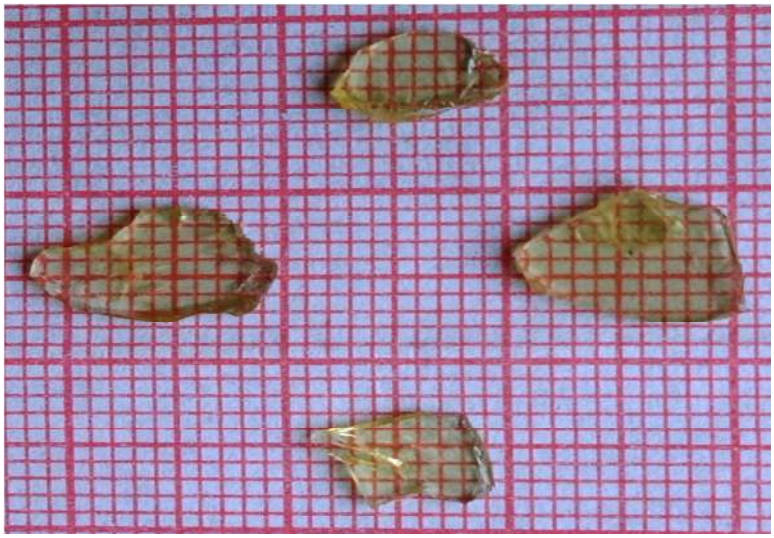

Fig. 2: Grown crystal of Piperazinium P-Aminobenzoate.

3. Results and Discussion

XRD Analysis

(i) The single crystal X-ray diffraction analysis is the powerful tool for determination of the structure of the crystal. The Piperazinium P-Aminobenzoate crystal belongs to orthorhombic crystal system with noncentrosymmetric space group $Pna2_1$. This space group satisfies one of the basic essential requirements of NLO material. The lattice parameters of the Piperazinium P-Aminobenzoate is found

to be a = 18.2964 Å, b = 7.1388 Å, c = 10.3574 Å, α = 90°, β = 90°, γ = 90° and volume V = 1352.83 $Å^3$. The structural parameters of the Piperazinium P-Aminobenzoate crystal were listed in the table 1.

Table 1: PZPAB crystal.

Crystal property	**Piperazinium P-Aminobenzoate**
Empirical formula	$C_4H_{11}N_2^+ \bullet C_7H_6NO_2^- \bullet H_2O$
Crystal system	Orthorhombic
Spacegroup	$Pna2_1$
Unit cell parameters	a = 18.2964 Å, b =7.1388 Å, c =10.3574 Å, α = 90°, β = 90°, γ = 90°
Volume of the unit cell	V = 1352.83 $Å^3$
Radiation wavelength	λ = 0.71073 Å

The crystalline nature of the Piperazinium p-aminobenzoic crystal was characterized by Powder x-ray diffraction analysis to reveal crystalline perfection of the compound. The x-ray diffraction spectrum of PZPAB was recorded using the X'pert PRO powder diffractometer with CuK_α radiation having the wavelength of λ = 1.5406 Å. The sample was scanned from the range of 10° to 80° at the rate of 2°/minute. The recorded powder x-ray diffraction spectrum is shown in Figure 3. The presence of sharp and well defined peaks confirms the good crystalline nature of piperazinium p-aminobenzoate crystal and the corresponding peaks were indexed. The sharp intense peaks are shown in the table 2.

FTIR Analysis

The FTIR spectrum was recorded to understand the chemical bonding and it provides useful information regarding the molecular structure of the compound. The KBr pellet technique was used to analyze the sample. FTIR spectrum was taken for the powdered sample in the wavelength range 4000-400 cm^{-1} using 380 FTIR Spectrophotometer having the resolution of 0.5 cm^{-1} and the spectrum of FTIR is shown in Figure 4.The observed FTIR is summarized in table 3.

Raman Analysis

Laser Raman spectrum was taken for the powdered sample in the wavelength range 4000-400 cm^{-1} using STR 500 mm focal length laser Raman spectrometer and the Raman spectrum is shown in the figure 5. Raman bands along with their vibrational assignments are summarized in table 4.

UV-Visible optical Absorption spectral analysis

The optical absorption spectral analysis of the grown PZPAB crystal was carried out using Perkin Elmer Lambda35 spectrometer between 250 and 800 nm. The absorption & transmittance spectrum of the as grown PZPAB crystal is shown in the Figure 6. The UV cut off wavelength of the crystal was found to be at 317 nm. The absence of absorption in the visible region suggests that the crystal possess the good nonlinear optical property.

Table 2: Peaks of XRD.

Pos. [°2Th.]	Height [cts]	FWHM Left [°2Th.]	d-spacing [Å]	Rel. Int. [%]
10.4002	121.43	0.1476	8.50603	3.53
13.5267	439.65	0.1476	6.54617	12.78
14.1626	173.47	0.1476	6.25365	5.04
15.1903	641.65	0.1476	5.83283	18.65
15.5192	252.21	0.0984	5.70992	7.33
17.0567	1184.78	0.1476	5.19854	34.44
19.5580	551.63	0.1476	4.53897	16.04
21.0129	470.57	0.1476	4.22787	13.68
21.5337	3439.78	0.1476	4.12679	100.00
23.8882	2086.44	0.1476	3.72510	60.66
24.8055	1168.61	0.1476	3.58939	33.97
26.3194	821.87	0.1476	3.38626	23.89
26.8804	317.96	0.1476	3.31685	9.24
27.4870	740.96	0.1476	3.24502	21.54
28.3924	145.42	0.1476	3.14356	4.23
29.4507	256.36	0.1476	3.03297	7.45
30.5232	719.77	0.1968	2.92879	20.92
31.3467	721.21	0.1476	2.85371	20.97
31.9957	276.41	0.1476	2.79729	8.04
32.4648	201.46	0.1968	2.75793	5.86
33.7596	164.56	0.1476	2.65506	4.78
34.3585	209.28	0.2952	2.61014	6.08
35.1350	131.82	0.1968	2.55421	3.83
35.6070	134.51	0.1476	2.52143	3.91
36.3967	554.72	0.1968	2.46852	16.13
37.9391	177.68	0.1476	2.37163	5.17
39.0984	130.54	0.2460	2.30395	3.80
39.5630	76.17	0.1476	2.27795	2.21
41.2584	89.98	0.3936	2.18818	2.62
41.8669	81.48	0.1476	2.15778	2.37
43.3737	77.32	0.1476	2.08624	2.25
43.8176	84.64	0.1476	2.06613	2.46
44.3690	117.18	0.1476	2.04173	3.41
45.0060	82.97	0.1968	2.01430	2.41
46.4121	73.75	0.1476	1.95650	2.14
48.0597	46.94	0.1968	1.89320	1.36
49.2598	48.17	0.1968	1.84985	1.40
50.7274	282.97	0.2460	1.79973	8.23
51.2972	67.33	0.1476	1.78107	1.96
52.5555	50.83	0.2460	1.74135	1.48
53.4279	22.86	0.2952	1.71496	0.66
54.1358	19.44	0.2952	1.69420	0.57
55.2169	25.97	0.3936	1.66356	0.76
56.6958	36.33	0.2952	1.62363	1.06
57.8343	32.12	0.5904	1.59435	0.93
60.7458	28.30	0.5904	1.52472	0.82

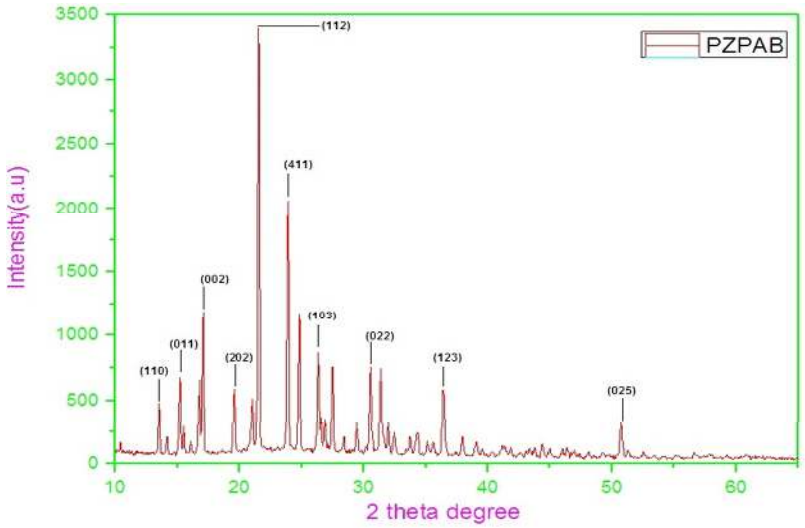

Fig. 3: Powder XRD pattern of PZPAB crystal.

Table 3: FTIR frequency assignments of PZPAB compound.

Functional groups	**Theoretical value**	**FTIR Experimental value**	**Assignments**
Amine	1200 – 1025	1089	C-N stretching alkyl
Amine	3500 – 3300	3327	N-H stretching
Alcohols	1200 – 1000	1123	C-O stretching
Carboxyl	1320 – 1210	1224	C-O stretching
Aromatics	3020 – 3000	3009	CH stretching
Aromatics	~1600	1609	C=C stretching

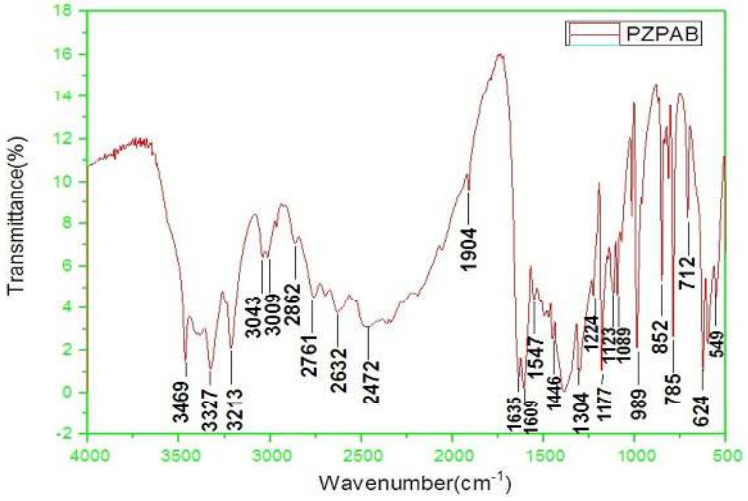

Fig. 4: FTIR spectrum of PZPAB.

Table 4: Raman frequency assignments of PZPAB compound.

Functional groups	Theoretical value	Laser Raman Experimental values	Assignments
Amine	1200 – 1025	1150	C-N stretching alkyl
Amine	3500 – 3300	3331	N-H stretching
Alcohols	1200 – 1000	1150	C-O stretching
Carboxyl	1320 – 1210	-----	C-O stretching
Aromatics	3020 – 3000	3077	CH stretching
Aromatics	~1600	1605	C=C stretching

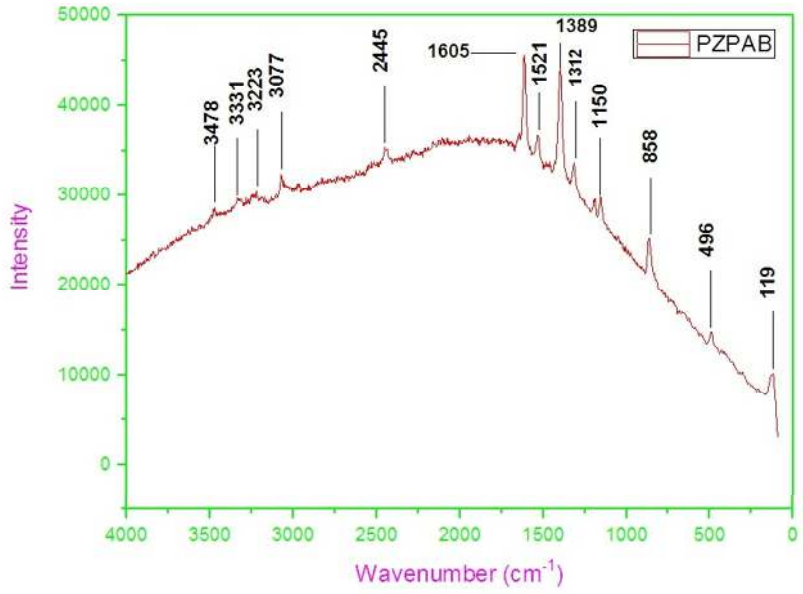

Fig. 5: Laser Raman spectrum of PZPAB.

UV-Visible optical Absorption spectral analysis

The optical absorption spectral analysis of the grown PZPAB crystal was carried out using Perkin Elmer Lambda35 spectrometer between 250 and 800 nm. The absorption & transmittance spectrum of the as grown PZPAB crystal is shown in the Figure 6. The UV cut off wavelength of the crystal was found to be at 317 nm. The absence of absorption in the visible region suggests that the crystal possess the good nonlinear optical property.

Photoluminescence studies

Photo luminescence spectroscopy is a non -destructive method for finding out the electronic structure and optical behavior. The Photoluminescence spectrum of the grown PZPAB was recorded in the wavelength region between 300 nm and 550 nm using RF-5301 spectrophotometer. The PL spectrum (Figure 7) of PZPAB grown crystal is excited at 350 nm. From the PL spectrum, one high intensity blue emission peak and one medium intensity violet emission peak was observed at 455 nm, 384 nm

respectively, and it attributes to shallow defects in the band gap and more ordered structure. The sharp high intensity caused because of the similar transition occurring at the various energy levels within the band gap.

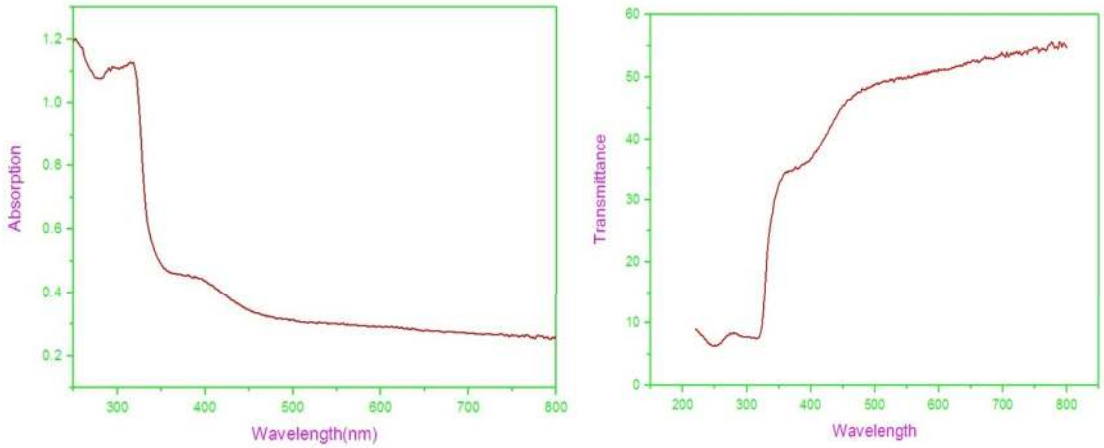

Fig. 6: UV-Visible absorption & transmittance spectrum of PZPAB.

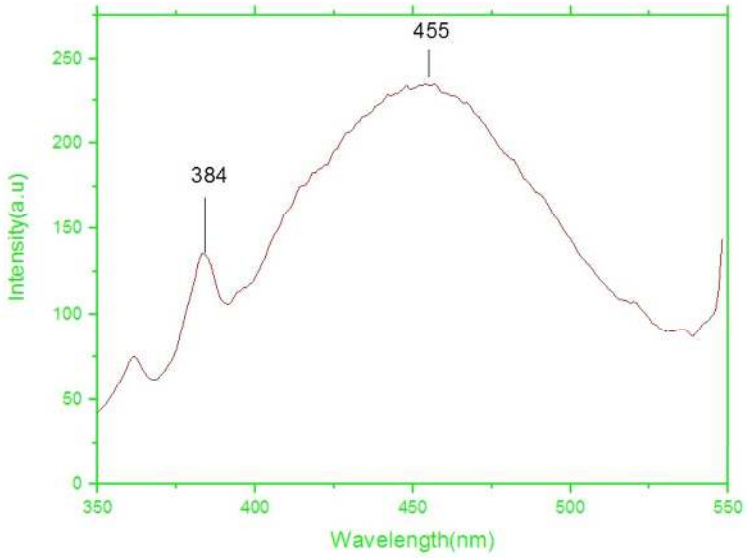

Fig. 7: Photoluminescence spectrum of PZPAB.

4. Conclusion

The piperazinium p-aminobenzoate crystal was successfully grown and characterized. The XRD pattern confirms the properties of NLO and the Raman and FTIR confirm all the functional groups. The UV and PL show the Optical properties. Thus, a good NLO crystal was successfully formed for LASER applications.

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