

ICMCT-2014 [10<sup>th</sup> – 12<sup>th</sup> March 2014]  
International Conference on Materials and Characterization Techniques

## Optical Studies of Polymorphic 2-Amino-5-Nitropyridinium Bromide

C. Indumathi<sup>1</sup> and S. Alfred Cecil Raj<sup>2\*</sup>

<sup>1</sup>Department of Physics, Bishop Heber College, Tiruchirapalli, India.

<sup>2</sup>Department of Physics, St Joseph's College, Tiruchirapalli, India.

\*Corres.author: sac63raj@gmail.com

**Abstract:** 2-amino-5-nitropyridinium bromide salt was synthesized by chemical reaction method. The single crystals of 2A5NPBr were grown by slow evaporation technique. Single crystal XRD shows that 2A5NPBr exhibit polymorphism and the identified space group of acentric and centric 2A5NPBr are  $P2_1$  and  $P2_1/a$  respectively. In the FTIR spectrum, vibrational bands observed around  $643\text{ cm}^{-1}$  confirms the presence of inorganic species  $\text{Br}^-$  found in 2A5NPBr respectively. UV-Vis studies shows that the material possess lower cut-off wavelength of 404 nm. The role of polymorphic nature of 2A5NPBr on the optical properties is discussed in detail.

**Keywords:** Organic; NLO; Polymorphism; SHG.

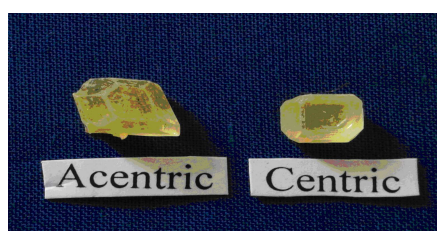
### Introduction and Experimental

Nonlinear Optical (NLO) materials play a vital role in advanced laser technology which are useful in high data storage, color displays, underwater communication, medical diagnostics[1,2]. A common and often productive route to identify efficient NLO materials is to utilize molecules with electron donating and accepting moieties attached to a conjugated system such as benzene or pyridine. Among the various organic molecules, 2-amino-5-nitropyridine (2A5NP) with herringbone motif allows for the growth of numerous salts, like 2-amino-5-nitropyridinium chloride (2A5NPCl), bromide (2A5NPBr), dihydrogen phosphate (2A5NPDP), dihydrogen arsenate (2A5NPDA) and tartrate (2A5NPT) [3,4]. These materials signify the role of counteranion, is important in obtaining crystal acentricity and the optimal packing of cations that induces large macroscopic quadratic nonlinearities.

Consequently, the design and preparation of new NLO-materials is complicated by polymorphism. The presence of polymorphic structures is also of crucial importance to the photonics applications and pharmaceutical industry, since polymorphs can have significantly different physical properties. Polymorphic systems can also provide excellent opportunities to study a chemical entity in more than one crystalline environment. 2A5NPBr is one such material with polymorphic nature and the crystal structure of its acentric and centric phase was already reported in literature [5]. In the present investigation, the role of polymorphism in the structural and optical properties of 2A5NPBr has been reported in detail.

The commercially available 2-amino-5-nitropyridine is a weak bronsted base and can acquire a proton ( $2A5NP^+$ ) in a strongly acidic aqueous medium. 2-amino-5-nitropyridinium bromide salt was synthesized by dissolving 2A5NP in hydrobromic acid solution at  $30^\circ\text{C}$  with the molar ratio 1:2 respectively. The content of the solution was stirred for 2 hours to yield a homogenous mixture and it was evaporated to dryness by heating below an optimum temperature of  $60^\circ\text{C}$ . By the addition of acetone, the salt crystallizes at room temperature as a light yellow microcrystalline powder. 2A5NPBr exhibits a positive solubility temperature gradient in water. Hence by solvent evaporation technique single crystals of 2A5NPBr were grown with  $\text{pH} = 2.04$ , at  $30^\circ\text{C}$ . Transparent single crystal of dimensions  $10 \times 8 \times 4 \text{ mm}^3$  was harvested after a typical period of 7 days and is as shown in Figure.1.

As inferred in literature, some difficulties emerged in the crystallization of 2A5NPBr, as it yields two phases in coexist during evaporation. Several trails have been made to obtain the precise conditions of crystallization of each phase by varying the growth condition (solvent, temperature and pH). Irrespective of the growth condition, coexistence of two phases could not be avoided. However many good quality crystals of each phase were obtained easily under this optimized condition.

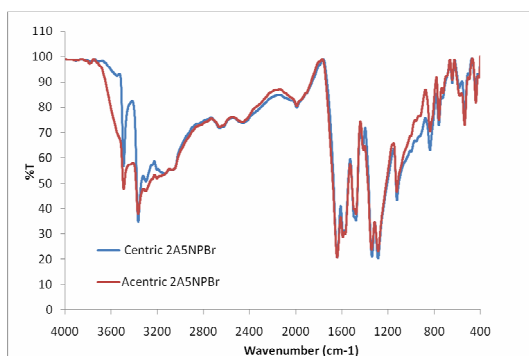
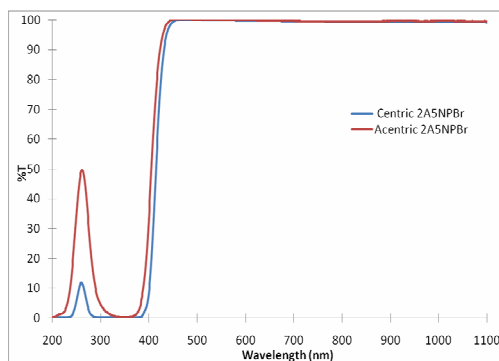


**Figure 1 :** As Grown Crystals of 2A5NPBr

## Results and Discussions

The cell dimensions of the carefully selected defect free single crystals of dimension  $0.3 \times 0.3 \times 0.3 \text{ mm}^3$  were identified by single crystal X-ray diffraction analysis using Enraf Nonius FR 590 diffractometer. Literature clearly shows that due to the polymorphic nature of 2A5NPBr, two phases coexist, the first was acentric  $P2_1$  and the other centric  $P2_1/a$ . As visual inspection of the sample does not always provide conclusive information about the phases of 2A5NPBr, several attempts of single X-ray diffraction have been recorded to distinguish the two phases of 2A5NPBr. The analysis reveals that 2A5NPBr with acentric space group, crystallizes with lattice parameters  $a = 10.023(5) \text{ \AA}$ ,  $b = 7.8009(4) \text{ \AA}$ ,  $c = 4.899(3) \text{ \AA}$ , and  $\beta = 94.89^\circ(4)$ . And centric crystals are identified to be  $a = 12.634(1) \text{ \AA}$ ,  $b = 7.894(2) \text{ \AA}$ ,  $c = 7.847(1) \text{ \AA}$ , and  $\beta = 91.12^\circ(3)$ . The volume of the unit cell of acentric and centric is found to be  $384.4(1) \text{ \AA}^3$  and  $772.53(4) \text{ \AA}^3$  respectively. These values agree very well with the reported values [5]. The reported crystal structures infer that when the N-N decreases beyond  $4 \text{ \AA}$ , the corresponding structure is centric. Hence in designing an efficient NLO material with donor acceptor system, care should be taken in attaining elongated N-N bond to obtain acentric structure in pyridine based molecules.

The Fourier Transform Infrared Spectrum of 2A5NPBr were recorded using JASCO 460 Plus FT-IR spectrometer. The vibrational bands corresponding to the grown acentric and centric single crystals of 2A5NPBr clearly shows that there is no much variation in the position of the observed peaks (Figure.2). Strong vibrational bands observed at  $3302$  and  $3300 \text{ cm}^{-1}$  indicate the presence of  $\text{NH}_2$  group vibrating at symmetrical modes for acentric and centric crystals, respectively. At  $1641$  and  $1640 \text{ cm}^{-1}$  the vibrational peak shows the presence of  $\text{C} = \text{N}$  in 2A5NPBr. The symmetric and asymmetric vibrational frequencies of  $\text{NO}_2$  occur at  $1571$ ,  $1571$ ,  $1342$  and  $1339 \text{ cm}^{-1}$  for acentric and centric system. The C-H out of plane bending occurs at  $758$  and  $759 \text{ cm}^{-1}$ . The vibrational band at  $643 \text{ cm}^{-1}$  for both the system, identifies the inorganic species  $\text{Br}^-$  found in 2A5NPBr. Hence FTIR reveals that there is no variation in the molecular structure due to polymorphic (acentric and centric) nature of 2A5NPBr.

**Figure.2** FTIR pattern of 2A5NPBr**Figure.3** Transmission spectrum of 2A5NPBr

The optical absorption and transmission spectrum were measured for both acentric and centric 2A5NPBr using VARIAN CARY 5E UV–Vis spectrophotometer. Both the phases possess a very low cut-off wavelength of 410 nm (Figure.3) which is short enough for the second harmonic generation (SHG) of Nd:YAG laser radiation at 1064nm or other applications in the green region [6]. The material with transparency window (410 - 1400 nm) shows a perceptible conclusion that the material can be a better entrant for nonlinear optical applications such as frequency doublers and optical limiters. As like molecular structure, linear properties observe no big variation due to polymorphism.

A preliminary study of the powder SHG measurements were performed using a modified Kurtz powder technique (Nd:YAG 1064 nm, 8 ns, 10 Hz) [7]. Single crystals of 2A5NPBr that crystallize in acentric space group is confirmed by the emission of green radiation ( $\lambda=532$  nm). The SHG efficiency of 2A5NPBr is compared with standard inorganic NLO material KDP and is found to be 1.2 times that of KDP and comparable to that of 2-methyl-2,4-dinitrophenyl aminopropanate (MNA). This efficiency is probably due to the density of the chromophores (75.7%), which is the highest observed among the herringbone structures built with 2A5NP entity. Thus it can be concluded that acentric 2A5NPBr is identified to be an efficient second order NLO material for the frequency conversion applications. Also the bond length of N-N of  $\text{NH}_2$  is very crucial in achieving the acentric phase and due to its variation the polymorphism arises in 2A5NPBr.

## References

1. Sabari Girisun T.C., Dhanuskodi S., Mater. Res. Bull. 2010, 45, 88.
2. Wang,X., Xu, D., Lu, M., Yuan, D., Huang, J., Cheng, X., Wang, S., Zhang, G.,Pan, M., Duan, X. and Yang, Z., Phys. Stat. Sol. (A) 2002, 191, 106.
3. Sasaki, T., Mori,Y., Yoshimura, M.J. Nonlinear Opt. Phys. Mater. 2001, 10, 249.
4. Zaccaro, J, Lonut, F, Ibanez, A. J. Mater.Chem. 1999, 9, 1091.
5. Pecaut, J, Levy, J.P, Masse, R, J. Mater.Chem., 1993, 3, 999.
6. Ibanez, A, Levy, J.P, Mouset, C, Prieur, E. J. Solid State Chem. 1997, 129, 22.
7. Kurtz, S.K, Perry, T.T. J. Appl. Phys. 1968, 39, 3798.

\*\*\*\*\*