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# Optical and spectroscopic studies of potassium p-nitrophenolate dihydrate crystal for frequency doubling applications

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#### ABSTRACT

Non centrosymmetric potassium p-nitrophenolate dihydrate single crystals have been grown by employing the technique of slow solvent evaporation from aqueous solution by slightly adjusting the pH and growth temperature. The grown crystals have been identified from single crystal XRD analysis, FTIR and FT Raman spectroscopic techniques. The high resolution X-ray diffraction experiments substantiate good quality of the title material. Between 510 and 2000 nm, the material is observed to be nearly transparent allowing it to be explored for potential use in device fabrication. In addition, the photoluminescence spectrum of the grown crystal at room temperature shows a stable broad violet-blue emission around the 383–550 nm wavelengths with the maximum centered at 436 nm. Owing to its excellent non linear figure of merit and strong PL emission, the title crystal can have technological applications in opto-electronic devices.

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#### 1. Introduction

Nonlinear optics is at the forefront of current research because of its importance in providing the key functions of frequency shifting, optical modulation, optical switching, optical logic, and optical memory for the promising technologies in areas such as telecommunications, signal processing, and optical interconnections [1-3]. Devices with enhanced figures of merit have developed over the last three decades as a major force to help drive nonlinear optics from the laboratory to real applications. The fast growing development of optical fiber communication systems has stimulated the search for better nonlinear materials capable of fast and efficient processing of optical signals. It has been demonstrated that organic crystals have large nonlinear susceptibilities compared with inorganic crystals, but their use in device fabrication is obstructed by low optical transparency, reduced mechanical properties, low laser damage threshold, and the inability to produce and process large single crystals [4,5]. Purely inorganic materials typically have excellent mechanical and thermal properties with relatively modest optical nonlinearities because of the lack of extended  $\pi$ electron delocalization. In semi-organic NLO crystals, however, polarizable organic molecules are stoichiometrically bonded with an organic host making them exhibit superior mechanical and

thermal properties which otherwise lack in organic materials. In recent years, the NLO properties of semi-organic complex products of p-nitrophenol have attracted great interest because these metal-organic complexes combine the high optical nonlinearity and chemical flexibility of organics with the physical ruggedness of inorganics [6–11]. The contribution from the delocalized  $\pi$  electrons belonging to the organic ligand results in high nonlinear optic and electro optic coefficients in this kind of materials. Potassium p-nitrophenolate dihydrate (NPK·2H<sub>2</sub>O) is one such semiorganic non linear material wherein the nitro group in the crystal lattice is bonded with the metal ion potassium through the conjugated  $\pi$ electron bond system of donor and acceptor ions, which provides high SHG efficiency of about 1.5 times than that of lithium nioboate [12].

Furthermore, solid state laser sources often use the association of a luminescent crystal and a SHG crystal. Recently there has been a great interest for self-doubling materials which exhibit both luminescence and nonlinear optical properties simultaneously. With the use of such crystals laser sources can be more compact [13–15]. In this paper, we present the growth of stable, optically transparent, NLO active NPK·2H<sub>2</sub>O single crystal by judiciously adjusting the pH and growth temperature employing slow solvent evaporation technique from aqueous solution. The FTIR and FT Raman spectra of NPK·2H<sub>2</sub>O are described on the basis of characteristic frequencies of the molecular groups – NO<sub>2</sub> and phenyl ring; they were compared to those of the similar aromatic nitro compounds. Consequently, for the assignment of peaks, we refer on one hand to our own experimental results and on the other hand to works treating similar

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The vibrational modes of NPK-2H<sub>2</sub>O single crystal and their tentative assignments.

IR (cm <sup>-1</sup> ) Raman (cm <sup>-1</sup> ) Ass		Assignment
-	539	NO <sub>2</sub> bending vibration (rocking)
618	-	Ring bending or stretching vibration
-	635	Ring bending or stretching vibration
700	-	Ring torsion
758	-	C-H out-of-plane symmetric deformation (wagging)
-	833	C-H out-of-plane bending
846	-	C-H out-of-plane bending
-	862	C-H out-of-plane bending
993	-	C-H in-plane bending
1110	-	C-H in-plane bending
-	1113	C-H in-plane bending
1170	-	C-H in-plane bending
-	1171	C-H in-plane bending
-	1321	NO <sub>2</sub> symmetric stretching
1332	-	NO <sub>2</sub> symmetric stretching
1458	-	NO <sub>2</sub> asymmetric stretching
-	1508	NO <sub>2</sub> asymmetric stretching
-	1531	NO <sub>2</sub> asymmetric stretching
1570	-	Ring bending or stretching vibration
-	1597	Ring bending or stretching + C-NO <sub>2</sub> vibration
1599	-	C–O stretching vibration
2852	-	C-H stretching vibration
2923	-	C-H stretching vibration
-	3057	C-H stretching vibration
3192	-	OH stretching vibration
3356	-	OH stretching vibration
3465	-	OH stretching vibration

compounds [16–18]. On the basis of such a comparison, in Table 1, we give a tentative assignment of the various modes observed in NPK·2H<sub>2</sub>O. HRXRD measurements substantiate reasonable quality of the grown crystal. Moreover, we demonstrate in the ensuing discussion that the title material exhibited strong violet-blue photoluminescence emission. On account of its outstanding non linear figure of merit and spectacularly good PL emission, the title crystal can have potential applications in opto-electronic devices.

#### 2. Experimental

#### 2.1. Material synthesis

The commercial reagent p-nitrophenol and potassium hydroxide pellets are dissolved thoroughly in a container in 1:1 stoichiometric ratio with millipore water as solvent. The solution was stirred well for about 48 h using a magnetic stirrer to ensure homogeneous concentration over entire volume of the solution. Efforts made to grow the crystals under supersaturation conditions (pH=8.54) at room temperature turned futile for not only it resulted in the growth of needle like crystals but also lost their transparency immediately after they were removed from the mother solution. After several test runs, we were able to grow transparent and stable single crystals of the title material after the pH of the solution and growth temperature were adjusted to be 7.54 and 323 K, respectively, by employing the technique of slow solvent evaporation. The grown crystal was then subjected to various characterization studies to elucidate its structural and optical properties. The photograph of the as grown single crystal is shown in Fig. 1.

#### 3. Results and discussion

#### 3.1. Single crystal XRD analysis

A carefully selected single crystal of NPK·2H<sub>2</sub>O was subjected to single crystal XRD analysis using an ENRAF NONIUS CAD-4 X-ray diffractometer. The X-ray diffraction study reveals that the crystal



Fig. 1. As grown single crystal of NPK-2H<sub>2</sub>O.

belongs to the non-centrosymmetric monoclinic crystal system and the lattice parameters are a = 22.195 Å, b = 3.870 Å, c = 21.291 Å, and  $\alpha = \gamma = 90^{\circ}$ ,  $\beta = 121.499^{\circ}$ , which are in good agreement with that of reported values in the literature [12].

#### 3.2. Morphology studies

Due to difference in the relative growth rate of crystal faces, crystals often present various morphological habits. For equilibrium of a steadily growing crystal, the growth rates of faces are evidently proportional to the distances from the crystal center to the respective *hkl* faces. In this case, the growth morphology may be predicted according to the relative growth rates of individual crystal faces. Morphology was measured using ENRAF NONIUS CAD4 diffractometer using  $\omega - 2\theta$  scan mode. The grown crystal presented a hexagonal morphology wherein it grows faster along [010] direction. The habit mainly consists of (010), (002), (200) and ( $\overline{2}02$ ) faces with (200) face well developed and more dominating. As a result the crystals have a shape extended in the [010] direction as shown in Fig. 2.

#### 3.3. FTIR and FT Raman analyses

The Fourier Transform Infra Red (FTIR) spectrum of the title material (Fig. 3) was recorded using KBr pellet technique between 450 and 4000 cm<sup>-1</sup> by Brukker IFS 66v FTIR spectrometer. FT Raman spectrum (Fig. 4) was recorded between 20 and 4000 cm<sup>-1</sup> at room temperature using a Bruker RFS 100/S FT Raman spectrometer. NO2 symmetric and asymmetric stretching vibrations of aromatic nitro group are observed at 1332 cm<sup>-1</sup> (IR) and 1458 cm<sup>-1</sup> (IR), respectively, in good agreement with the values given in the literature [12]. The symmetric C-H vibrations of the out-of-plane deformation (wagging) are identified in the IR spectrum at  $758 \,\mathrm{cm}^{-1}$ . The Raman band at 539 cm<sup>-1</sup> can be assigned to the NO<sub>2</sub> bending vibration (rocking). In accordance with the various data published in the literatures [16,17], the bands at  $618 \text{ cm}^{-1}$  and  $700 \text{ cm}^{-1}$  in the IR spectrum are assigned to the bending or stretching vibrations of the ring and to its torsion vibrations, respectively. However, the band at 646 cm<sup>-1</sup> in the IR spectrum assigned to the C-NO<sub>2</sub> and C-O stretching and ring bending or stretching vibrations in NPNa [18] is not well resolved in NPK-2H<sub>2</sub>O. The IR band at  $846 \text{ cm}^{-1}$ (862 cm<sup>-1</sup> in Raman) is attributed to the C-H out-of-plane bending. The vibrational modes corresponding to the C-H in-plane bending were observed in the IR spectrum at 993, 1110 (1113 cm<sup>-1</sup> in Raman) and at 1170 cm<sup>-1</sup>(1171 cm<sup>-1</sup> in Raman), respectively.



Fig. 2. Morphology of NPK-2H<sub>2</sub>O.

The bands at  $1570 \text{ cm}^{-1}$  in IR or at  $1597 \text{ cm}^{-1}$  in Raman and at  $1599 \text{ cm}^{-1}$  in IR are assigned to ring bending or stretching vibration and ring bending or stretching plus C–NO<sub>2</sub> and C–O stretching vibrations, respectively. In the infrared, the C–H stretching vibration bands of the aromatic ring appear at  $2852 \text{ cm}^{-1}$  and  $2923 \text{ cm}^{-1}$  while it produce a peak at  $3057 \text{ cm}^{-1}$  in the Raman spectrum. There is a broad envelope carrying peaks due to OH stretch at 3465,  $3356 \text{ and } 3192 \text{ cm}^{-1}$ , respectively, due to hydrogen-bonded lattice water. The 1,4-di substitution is revealed by the peak at  $843 \text{ cm}^{-1}$ . The presence of hydrates of potassium metal ion is confirmed by the peak at  $485 \text{ cm}^{-1}$  in IR [12] and at  $496 \text{ cm}^{-1}$  in Raman spectrum. Moreover, there are no well defined peaks in the Raman spectrum between  $1672 \text{ and } 3000 \text{ cm}^{-1}$  and between  $3100 \text{ and } 4000 \text{ cm}^{-1}$ .



Fig. 3. Fourier Transform Infra Red Spectrum.



Fig. 4. FT Raman spectrum of NPK-2H<sub>2</sub>O single crystal.

However, the very weak Raman bands at 129, 187 and 262 cm<sup>-1</sup> are assigned to the hydrogen bonds in accordance with the values available in the literatures [16].

#### 3.4. High-resolution X-ray diffraction analysis

A multicrystal crystal X-ray diffractometer designed and developed at National Physical Laboratory [19] has been used to study the crystalline perfection of the grown single crystal. Fig. 5 shows the high-resolution diffraction curve (DC) recorded for the grown NPK·2H<sub>2</sub>O single crystal along (200) planes using symmetrical Bragg geometry by employing the multicrystal X-ray diffractometer with MoK $\alpha_1$  radiation. The solid line (convoluted curve) is well fitted with the experimental points represented by the filled circles. On deconvolution of the diffraction curve, it is clear that the curve contains an additional peak, which is 51 arcs away from the main peak. This additional peak depicts an internal structural very low angle boundary. As seen in Fig. 5, two regions of the crystal are misoriented by a finite angle  $\alpha$  also known as tilt angle. The two regions may be perfect. If the value of  $\alpha$  is  $\leq 1$  arc min, we may call it as very low angle boundary. If  $\alpha > 1$  arc min but less than a degree, we call it as low angle boundary. For more details of such structural grain boundaries including their affect on physical properties, reference is made available elsewhere [20,21]. The angular separation



Fig. 5. Diffraction curve recorded for NPK-2H<sub>2</sub>O single crystal.



Fig. 6. UV-vis-NIR absorption spectrum.

between the two peaks gives the tilt angle  $\alpha$  which is 40 arcs for the specimen as seen in the figure. The FWHM (full width at half maximum) of the main peak and the very low angle boundary are 20 and 82 arcs respectively. These low values reveal the fact that both the regions of the crystal are nearly perfect as one can expect such low values only for crystals with reasonable quality. Though the specimen contains a very low angle boundary, the relatively low angular spread of around 200 arcs of the diffraction curve and the low FWHM values show that the crystalline perfection is reasonably good. Thermal fluctuations or mechanical disturbances during the growth process could be responsible for the observed very low angle boundary. It may be mentioned here that such very low angle boundaries (which may hardly deteriorate the properties) could be detected with well resolved peaks in the diffraction curve only because of the high-resolution of the diffractometer, characterized by very low values of wavelength spread i.e.  $\Delta\lambda/\lambda$  and horizontal divergence for the exploring or incident beam, which are, respectively, around 10<sup>-5</sup> and much less than 3 arc s of the multicrystal X-ray diffractometer used in the present studies.

#### 3.5. UV-vis-NIR absorption studies

Absorption spectrum is very important for any NLO material because a nonlinear optical material can be of practical use only if it has wide transparency window. Hence, to assess its suitability for NLO applications, the grown single crystal with a thickness of about 2 mm was subjected to UV-vis-NIR studies at room temperature in the wavelength range from 200 to 2500 nm using a Varian Cary 5E UV-vis-NIR spectrometer. As seen in Fig. 6, between 510 and 2000 nm, the material is observed to have low absorption and better transparency. Although this crystal has a lower optical cut off at 510 nm, it is still better compared to those of 3-methyl-4-methoxy-40-nitrostilbene (MMONS) [22] and m-nitroaniline (m-NA) [23], with lower optical cut offs at 520 nm and 515 nm, respectively. The low absorption in the entire region from 510 nm to 2000 nm enables it to be a good candidate for electro-optic and NLO applications. Just below 510 nm, the absorbance raises more than four units. This is due to the electronic transitions in the aromatic ring of the title material.

#### 3.6. Determination of optical band gap

The variation of optical absorption coefficient ( $\alpha$ ) with photon energy (hv) was found to obey this relation:

$$\alpha = \frac{2.303A}{t} \tag{1}$$



**Fig. 7.** Variation of photon energy (hv) with  $(\alpha hv)^2$ .

where A is the absorbance and t the thickness, neglecting the reflection coefficient, which is negligible and insignificant near the absorption edge. The relation between  $\alpha$  and  $E_g$  for a direct transition is given by

$$(\alpha h\nu)^2 = A(E_g - h\nu) \tag{2}$$

where  $E_g$  is the optical band gap of the crystal and A is a constant. The variation of  $(\alpha hv)^2$  with hv in the fundamental absorption region is plotted in Fig. 7. The band gap of the crystal can be evaluated by extrapolation of the linear part which is found to be 5.1 eV. The wide band gap of the title material confirms the large transmittance in the visible region.

#### 3.7. Photoluminescence studies

Fluorescence may be expected generally in molecules that are aromatic or contain multiple conjugated double bonds with a high degree of resonance stability. Hence the emission spectrum of NPK·2H<sub>2</sub>O was recorded using JOBIN YVON FLUROLOG-3-11 spectroflurometer at room temperature and is shown in Fig. 8. It exhibited distinct violet-blue photoluminescence with the emission peaks at 410, 436 and 461 nm on excitation at 354 nm. It is found that the emission peak intensity decreases quickly after 461 nm. Moreover, the PL emission from NPK·2H<sub>2</sub>O is found to be quite strong compared to sodium p-nitrophenolate dihydrate single crystal reported elsewhere [24]. Such a strong PL signal is an indicator of high quality surface [25]. The strong PL emission of the title material may find potential applications in optoelectronic devices [26].



Fig. 8. Photoluminescence spectrum of NPK·2H<sub>2</sub>O single crystal.

#### 4. Conclusions

Good optical quality single crystals of NPK·2H<sub>2</sub>O have been grown by adjusting the growth parameters employing the technique of slow solvent evaporation from its aqueous solution. Single crystal XRD analysis, FTIR and FT Raman spectroscopic studies confirm the identity of the title material. High resolution XRD measurements substantiate reasonably good quality of the grown single crystal. Between 510 and 2000 nm, the material is observed to be nearly transparent making the material suitable for non linear optical applications. The band gap of the material was found to be 5.1 eV from UV absorption data. Although the investigation of the properties of NPK·2H<sub>2</sub>O is still in progress, NPK·2H<sub>2</sub>O crystal can be expected to have potential applications in opto-electronic devices in view of its excellent non linear figure of merit and strong PL emission.

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