Structure-Property Relationship in Nonlinear Optical and Micro Hardness Study of Anilinium Dihydrogen Phosphate of 2-Amino-6-Methyl Pyridinium Phosphate Crystals

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Abstract

Anilinium Dihydrogen Phosphate (ADHP) and 2-amino-6-methylpyridinium phosphate (2A6MPP) crystals were synthesized via the solution method and compared for their mechanical and optical properties. ADHP crystals demonstrated superior nonlinear optical (NLO) performance with a higher nonlinear absorption coefficient of 2.308×10^{-4} m/W and a third-order nonlinear susceptibility of 0.983×10^{-6} esu. Additionally, ADHP exhibited greater mechanical strength, making it more durable for practical applications. In contrast, 2A6MPP crystals, while displaying NLO properties, showed lower hardness and were classified as softer materials (Meyer's index: 2.6142). The findings confirm ADHP's enhanced suitability for advanced optoelectronic and nonlinear optical applications, outperforming 2A6MPP in both mechanical and optical performance.

Introduction

Nonlinear optical (NLO) materials have garnered significant attention due to their wide range of applications, including optoelectronics, second harmonic generation (SHG) devices, signal processing, optical communication, and optical computing. NLO materials are categorized into organic, inorganic, and semiorganic crystals, each offering distinct advantages and limitations. Semiorganic NLO crystals, which result from combining organic and inorganic components in specific proportions, exhibit unique physical and chemical properties that blend the characteristics of both material types [1-3]. The successful combination of high nonlinear optical coefficients from organic molecules with the exceptional physical properties of inorganic materials has yielded promising results in recent years. These semiorganic crystals demonstrate high damage thresholds, broad transparency ranges, low deliquescence, and elevated nonlinear coefficients, making them suitable for device fabrication [4, 5].

In this study, anilinium dihydrogen phosphate and 2-amino-6-methylpyridinium phosphate (2A6MPP), a semiorganic NLO crystals, were synthesized using the solution growth method. Numerous other anilinium-based crystals, including anilinium nitrate, anilinium picrate, anilinium hydrogen phosphite, and anilinium hydrogenoxalate hemihydrate, have been studied extensively [6-8]. Aromatic amines, particularly aniline and its derivatives, play crucial roles in biology and chemical industries, where they are used in dye production, pesticides, and antioxidants [9-13]. Aniline has also been investigated for its applications in electrical conductivity, electroluminescence, rechargeable batteries, and anti-corrosion technologies. Several other aniline-based NLO crystals, such as P-nitro aniline-l-tartaric acid, 4-nitro-4-methoxy benzylidene aniline, 2-methoxyanilinium nitrate, and 3-nitro aniline, have been synthesized and reported in the literature. Single crystals of 2A6MPP were grown using the solution method in a mixed ethanol-water solvent, followed by extensive characterization to analyze their suitability for practical applications.

Growth of crystals

Preparation of ADHP Single Crystal

High-purity aniline and orthophosphoric acid were procured from Merck India for the crystal growth experiment. A 1:1 molar ratio of these reactants was dissolved in a mixed solvent of ethanol and double distilled water (1:1 ratio) to form a saturated solution. The solution was heated and stirred for two hours, then filtered. The filtered solution was placed in a growth vessel, covered, and left undisturbed for slow evaporation. After approximately 20 days, crystals of anilinium dihydrogen phosphate (ADHP) formed and were harvested. The ADHP single crystal formation process shown in Fig. 1

Figure 1 Preparation Steps of ADHP Single Crystal

Preparation of 2A6MPP Single Crystal

Analytical grade 2-amino-6-methylpyridine (98%) and orthophosphoric acid (99%) were obtained from Merck India and used in a 1:1 molar ratio for the synthesis of 2-amino-6-methylpyridinium phosphate (2A6MPP). The reactants were dissolved in a mixed solvent of ethanol and double distilled water (1:1 by volume) and stirred at 35°C for 4 hours to achieve a homogeneous solution, shown in Fig. 2. After filtering, the solution was placed in a growth vessel covered with a perforated sheet to allow slow evaporation. Over 25 days, 2A6MPP crystals formed, and these were harvested for further analysis.

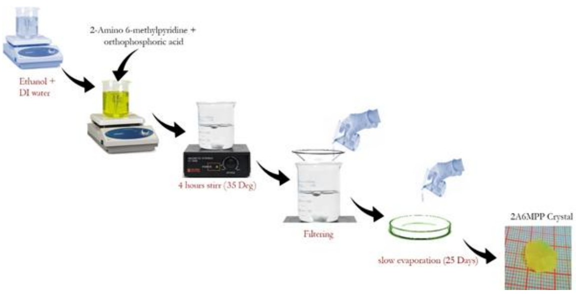

Figure 2 Step by Step Preparation Process of 2A6MPP Single crystal

Results and discussion

Lattice Constants and Crystal Structure

The grown ADHP crystal was analyzed using a Bruker Kappa Apex II X-ray diffractometer with Mo Kα radiation, based on Bragg's law (2d sin Θ = nλ). A high-quality ADHP crystal (0.4 x 0.5 x 0.3 mm³) was used for single crystal XRD, revealing triclinic structure with space group P-1 and lattice parameters: a = 8.793(4) Å, b = 10.426(2) Å, c = 14.147(2) Å, α = 87.03(2)°, β = 74.94(5)°, γ = 84.25(3)°, V = 1244.54(4) Å³, Z=6. The centrosymmetric nature of the P-1 space group indicates no SHG, though ADHP exhibits third harmonic generation, suitable for UV laser generation, with lattice constants closely matching literature values [14]. A well-formed 2A6MPP crystal (0.5 x 0.5 x 0.3 mm³) was used to determine its lattice parameters and crystal structure.

Z-Scan Studies

Z-scan studies were performed to investigate the third-order nonlinear optical (NLO) properties of ADHP and 2A6MPP crystals. Both open and closed aperture methods were used with a He-Ne laser (λ = 632.8 nm) as the light source. For ADHP, the closed aperture Z-scan curve showed a pre-focal transmittance peak followed by a post-focal valley, indicating a self-defocusing nature, with a nonlinear refractive index of -4.937 x 10^{-11} m²/W (Fig. 3 (a)). The open aperture curve demonstrated multi-photon absorption behavior, yielding a nonlinear absorption coefficient of 2.308 x 10^{-4} m/W. The third-order nonlinear susceptibility was calculated to be 0.983 x 10^{-6} esu, making ADHP suitable for optical sensor protection (Fig. 3 (b)) [15-17].

In comparison, 2A6MPP also displayed a self-defocusing nature, with a nonlinear refractive index of -8.026 x 10^{-11} m²/W. However, its nonlinear absorption coefficient was higher at 5.732 x 10^{-4} m/W, and the third-order nonlinear susceptibility was 8.474 x 10^{-7} esu. Despite 2A6MPP showing a larger nonlinear susceptibility, ADHP outperforms it in terms of lower absorption coefficient and better suitability for applications like optical sensor protection due to its higher stability and balanced NLO properties (Fig. 3 (c & d)) [18-21].

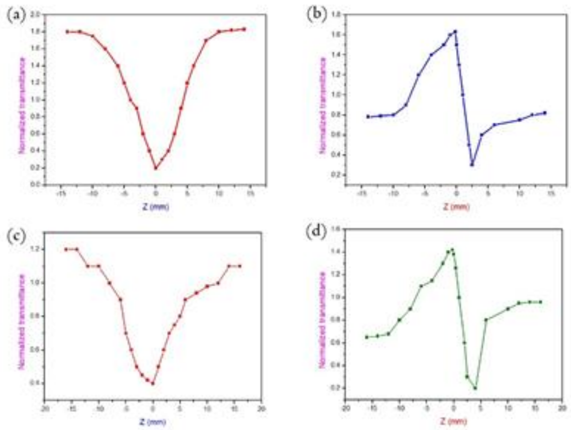

Figure 3 (a) Open Aperture and (b) Closed Aperture Z-scan curve for ADHP Crystal, (c) Open Aperture and (d) Closed Aperture Z-Scan Curve for ADHP Single Crystal

UV-visible Spectral Studies

UV-visible spectroscopy was used to analyze the optical properties of ADHP and 2A6MPP crystals. For ADHP, the lower UV cut-off wavelength was observed at 215 nm with high transmittance in the visible region, making it highly suitable for optoelectronic applications (Fig. 4 (a)). The absorption in the 250–350 nm range was attributed to π–π* and n–π* transitions, and the optical band gap was determined to be 5.75 eV (Fig. 4 (b)). This large band gap further confirms its potential for NLO applications [22-25].

In comparison, 2A6MPP exhibited a UV cut-off wavelength at 220 nm, with low absorption and high transmittance in the visible and near-infrared regions. The optical band gap for 2A6MPP was slightly lower at 5.62 eV (Fig. 4 (c & d)). While 2A6MPP demonstrates suitability for SHG generation, the higher band gap and superior optical transparency of ADHP make it a more promising candidate for NLO and optoelectronic applications. Additionally, ADHP's better performance in the UV region highlights its advantage over 2A6MPP for advanced optical uses [26, 27].

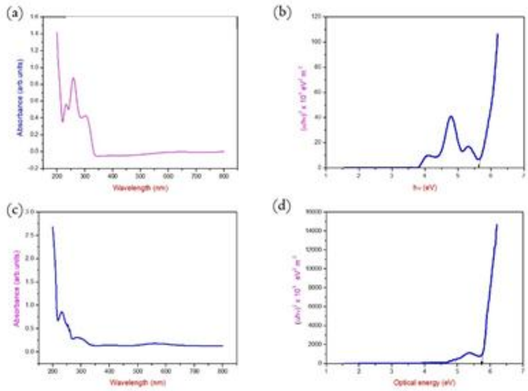

Figure 4 (a) Absorbance curve and (b) Tauc's plot for ADHP crystal, (c) Absorbance curve and (d) Tauc's plot for ADHP single crystal

Microhardness Studies

Microhardness studies were conducted on ADHP and 2A6MPP crystals to assess their mechanical properties. For ADHP, the Vickers hardness number increased with applied load due to the reverse indentation size effect. Cracks appeared when loads exceeded 100 g, indicating a strong resistance to deformation. The work hardening coefficient for ADHP was found to be 2.8325 (Fig. 5 (a & b)), and the calculated yield strength was in the range of 10^6 Pa. The elastic stiffness constant was also high, on the order of 10^{15} Pa, confirming ADHP as a mechanically robust material suitable for device fabrication.

In comparison, 2A6MPP showed an increase in hardness with applied load, but its work hardening coefficient of 2.6142 indicated that it is a softer material (Fig. 5 (c & d)). Cracks also appeared at loads above 100 g, and the corrected hardness value (Ho) was low at 0.00575 g/m². The negative resistance pressure confirmed the reverse indentation size effect, but overall, ADHP demonstrated superior mechanical strength, with higher yield strength and stiffness, making it more suitable for applications requiring mechanical durability [26, 27].

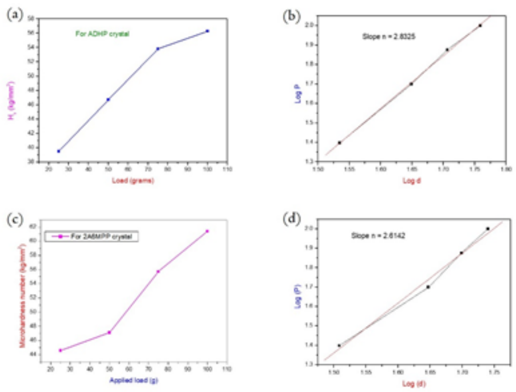

Fig. 5. (a)Variation of hardness with applied load and (b) Plot of log P versus log d for ADHP crystal, (c) Variation of hardness with applied load (d) Plot of log P versus log d for 2A6MPP crystal

Conclusions

Anilinium dihydrogen phosphate (ADHP) crystals, grown by the solution method, showed superior properties compared to 2-amino-6-methylpyridinium phosphate (2A6MPP) crystals. ADHP exhibited a higher nonlinear absorption coefficient (2.308×10^{-4} m/W), better third-order nonlinear susceptibility (0.983×10^{-6} esu), and stronger mechanical strength. While both materials displayed nonlinear optical properties, 2A6MPP had a lower hardness, a softer nature (Meyer's index of 2.6142), and lower corrected hardness. Overall, ADHP's enhanced mechanical and optical performance makes it more suitable for advanced optoelectronic applications.

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