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Influence of Acetic Acid on the Optical Characteristics of Potassium Dihydrogen Phosphate Doped Crystal

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Potassium dihydrogen phosphate (KDP) single crystals doped with acetic acid (AA) were synthesized using the slow evaporation solution technique. This study investigates the effects of 1M acetic acid doping on the optical properties of KDP crystals, focusing on optical transmittance, optical band gap, and optical constants using UV–Visible spectroscopy. The results revealed a significant improvement in the optical transparency of doped crystals, with transmittance increasing from 60% in pure KDP to 80% in doped samples. The optical band gap also increased from 5 eV in pure KDP to 5.3 eV in acetic acid-doped KDP. Furthermore, doped KDP crystals demonstrated reduced refractive index and decreased reflectance, which are advantageous for optical coatings and photonic devices. Photoluminescence studies showed strong violet emission centered at 358 nm, indicating high optical quality. Additionally, second harmonic generation (SHG) efficiency was enhanced by 1.39 times compared to undoped KDP crystals, demonstrating the material's suitability for nonlinear optical (NLO) applications. The structural analysis using XRD confirmed the tetragonal structure of both pure and doped KDP crystals, with minor changes in lattice parameters and unit cell volume. These improvements make acetic acid-doped KDP crystals highly promising candidates for advanced optoelectronic and laser frequency conversion systems. The study highlights the significant role of organic acid doping in enhancing the functional performance of KDP crystals and suggests their potential application in photonic and electro-optic devices.

Keywords: KDP crystal, doping, acetic acid, optical properties, UV-visible spectrum.

1. Introduction

A basic inorganic nonlinear optical material with good optical, dielectric, and thermal properties, potassium dihydrogen phosphate is essential to the study of second harmonic generations and the optoelectronics branch [1]. High optical homogeneity, an outstanding cubic susceptibility (χ3) of about 10−14 esu, and a notable SHG coefficient (d36 = 0.39 pm/V) are the characteristics of these crystals [2]. Regarding optoelectronics, telecommunications, laser technology, and other disciplines where nonlinear optical effects are used, its high transparency in the UV-visible band can be helpful for NLO applications. Because of their nonlinear responses to bright light, these materials' optical characteristics vary depending on how intense the incident light is. It is a well-9known inorganic NLO material that has good thermal, optical, and dielectric properties. It is a frequent procedure to dope KDP crystals with organic compounds in order to increase their nonlinear optical response or adjust their properties for particular uses. Enhancement of NLO characteristics can result from doping an organic substance into the KDP crystal lattice, as this can introduce new energy levels and modify the crystal shape [3]. Recent research has demonstrated the important role that organic additives—especially carboxylic acids like formic acid, oxalic acid, and maleic acid—play in improving the optical, mechanical, and electrical properties of KDP crystals, which is essential for the manufacture of devices.

2. Materials and Methods

To yield a supersaturated potassium dihydrogen phosphate solution at room temperature, high grade Merck manufacture KDP salt was steadily dissolved in deionized water time to time. The beaker containing the supersaturated solution of KDP material was filled with a carefully determined amount of 1 mole of acetic acid. For 4 to 5 hours, the KDP solutions containing 1 mol of acetic acid were stirred to ensure uniform doping throughout the mixture. Using Whatmann's filter paper No. 1, the solution was filtered in a beaker that had been rinsed. To enable the gradual solvent evaporation at 320 C, the filtered solution was maintained in an isolated, vibration-free, constant temperature bath. It took 7-8 days to harvest the transparent crystal.

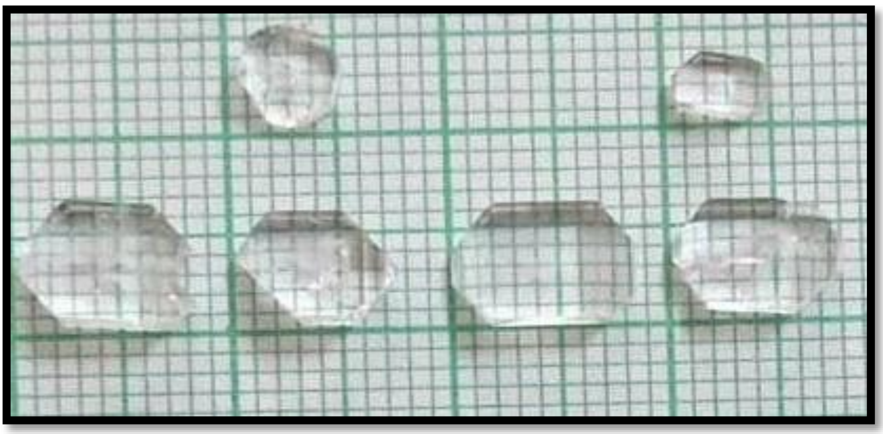

Figure 1: KDP doped ACETIC ACID (AKC)

3. Results and Discussion

UV-Visible Spectrophotometer

Materials exhibiting remarkable optical capabilities in the visible band have led to a significant demand for devices providing UV-tunable lasers as laser frequency conversion techniques [11]. Devices supporting UV-tunable lasers and laser frequency conversion systems are in high demand due to materials that exhibit exceptional optical performance in the visible spectrum [11]. We used the Shemadzu UV-2450 spectrophotometer to capture the UV–visible transmittance spectrum data of both pure and acetic acid doped KDP crystals in the 200–900 nm range. The spectrum shows that over the whole visible range,the optical transparency of the KDP crystal doped with acetic acid is substantially higher than that of KDP. It is found that the transmittance (T) of the KDP crystal is 60% when the dopant is absent and 80% when the dopant is acetic acid. A superior parameter that is desirable for the effective transmission of SHG radiation from Nd:YAG lasers and NLO devices is the improved transparency of doped KDP crystals [12]. The tauc's figure was created using the equation that shows the connection between the material's absorption coefficient (α) and optical band gap (Eg). The study revealed that the completely natural and acetic acid doped KDP crystals have optical band gaps of 5 and 5.3 eV, respectively. We find that the KDP crystal's band gap value has increased with the integration of acetic acid dopant. This studies doped KDP crystals demonstrate good transmittance across a broad wavelength range, as do the crystals with greater Eg values [13]. Therefore, the doped KDP crystals are perfect for optoelectronic devices because of their increased band gap value as well as high transmission [14]. Figure 8 and 6 show the visible area refractive index along with reflectance properties of pure and doped KDP crystals, respectively. When it comes to coatings used to lessen reflection in thermal solar devices, doped KDP crystals show significantly reduced refractive index along with reflectance than unaltered KDP crystals [15-17]. For the purpose of measuring the performance of photonic devices including optical filters, resonators, and reflectors, the acetic acid doped KDP crystal, which has a reduced refractive index, is highly significant [18]. The KDP crystal's great optical transparency, reduced refractive index, and decreased reflectance all suggest that the dopant has mostly inhibited the growth of point and line defects [19]. The primary prerequisite for creating electro-optic modulators is the acetic acid doped KDP crystal's exceptional optical uniformity [18-19].

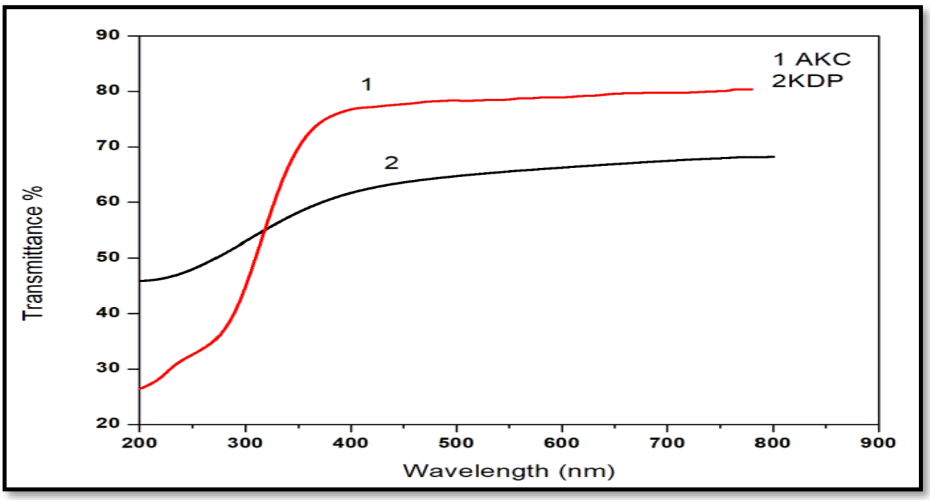

Figure 2: UV-VIS Spectral analysis of pure and KDP doped Acetic Acid

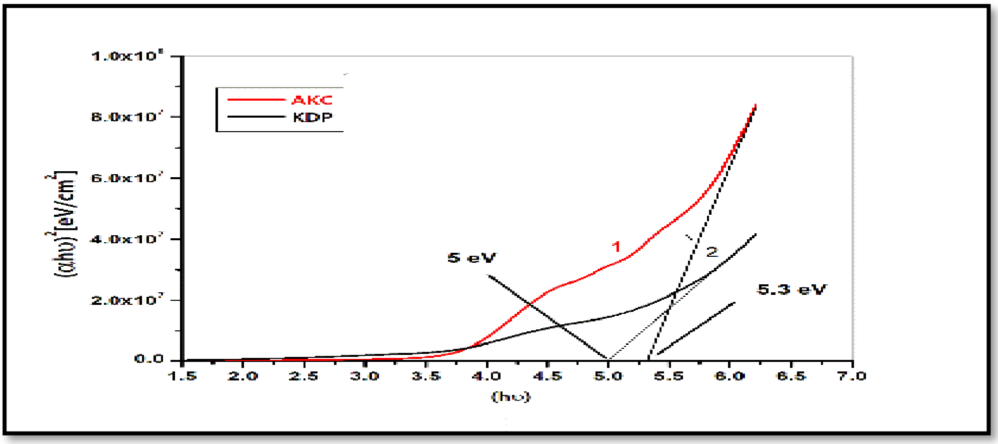

Figure 3: Tauc's graph

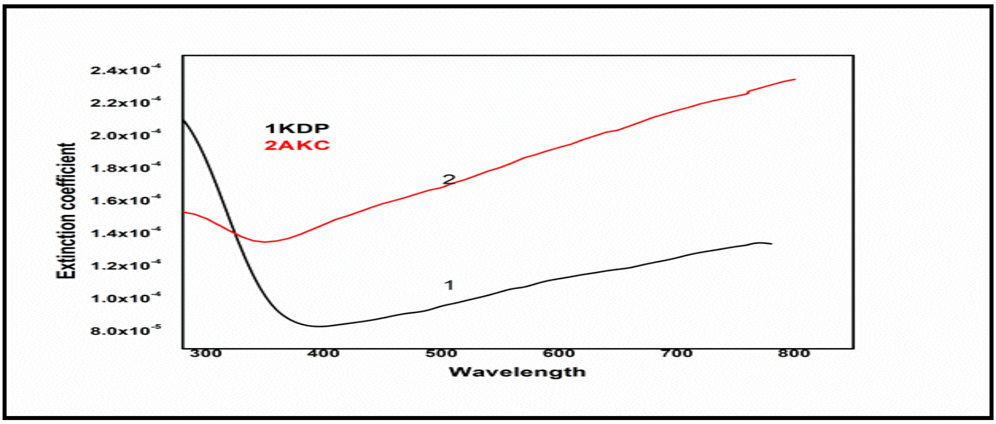

Figure 4: Extinction Coefficient vs.Photon energy (eV)

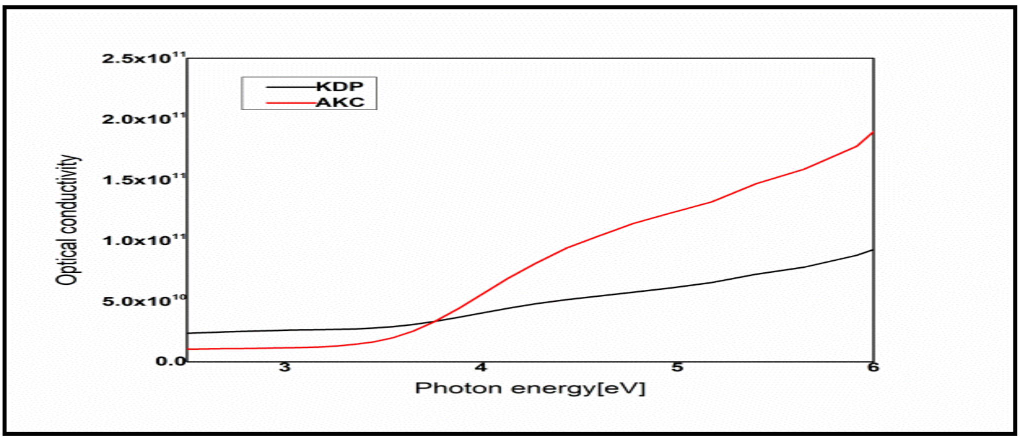

Figure 5: Optical Conductivity vs. photon energy (eV)

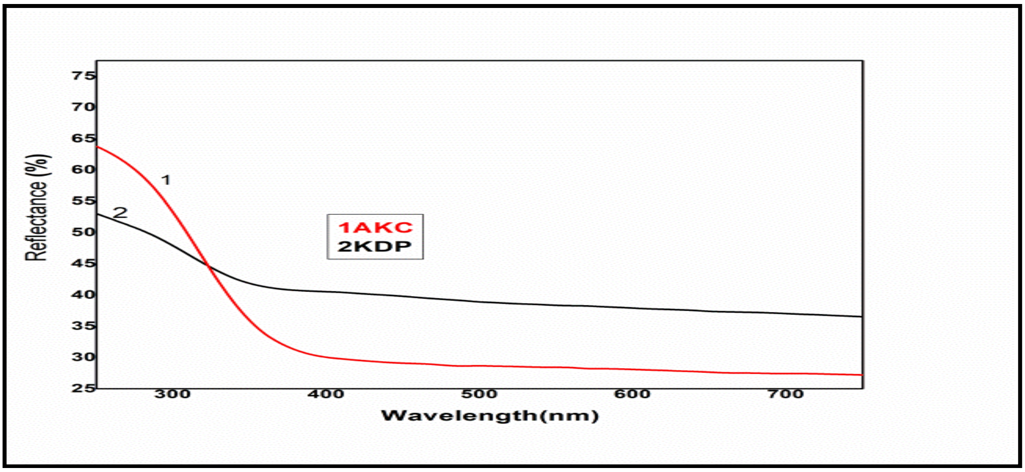

Figure 6: Reflectance (%) Vs Wavelength (nm)

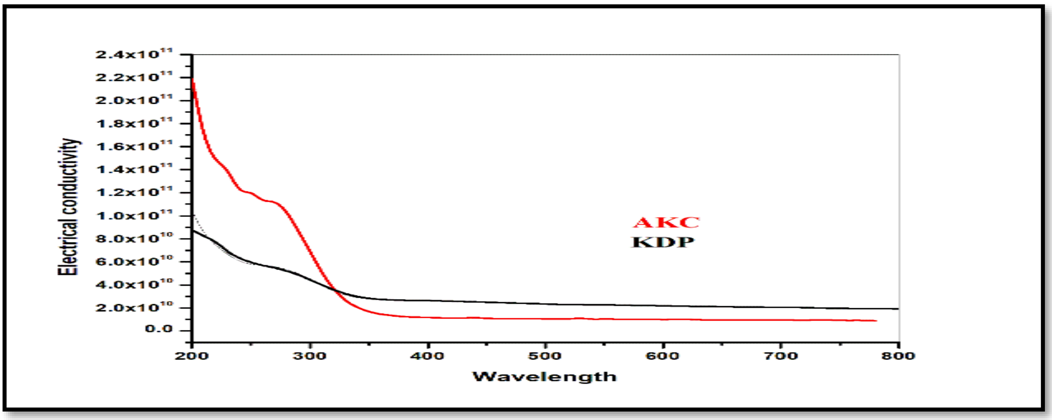

Figure 7: Electrical Conductivity Vs Wavelength (nm)

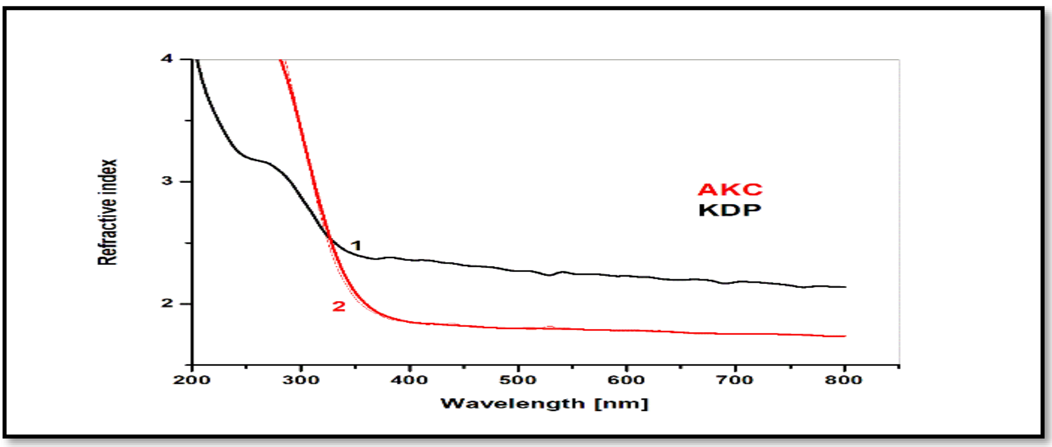

Figure 8: Refractive Index vs. Wavelength (2)

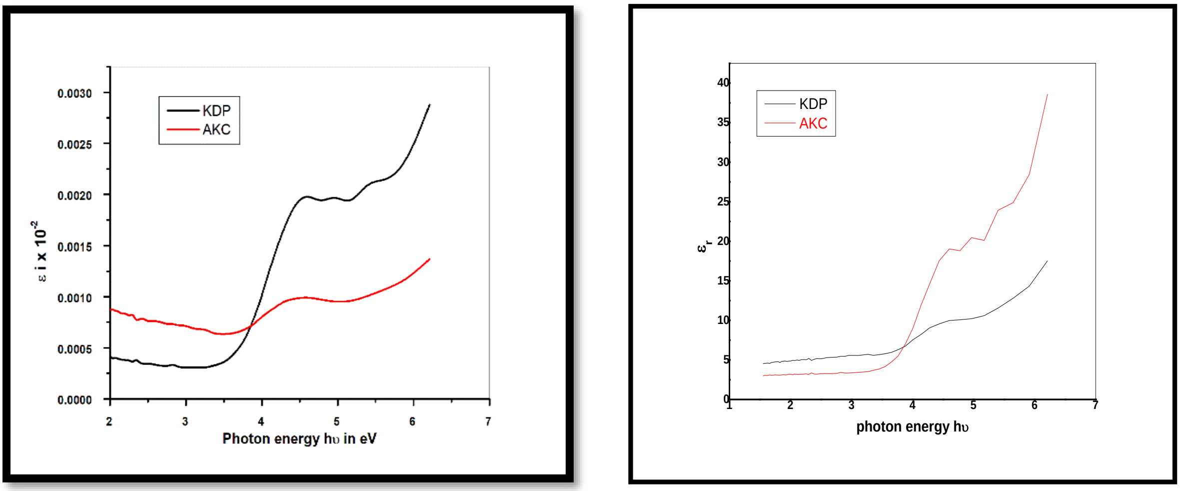

Figure 9 (a+b): Real and Imaginary Parts of Dielectric vs. photon Energy (eV)

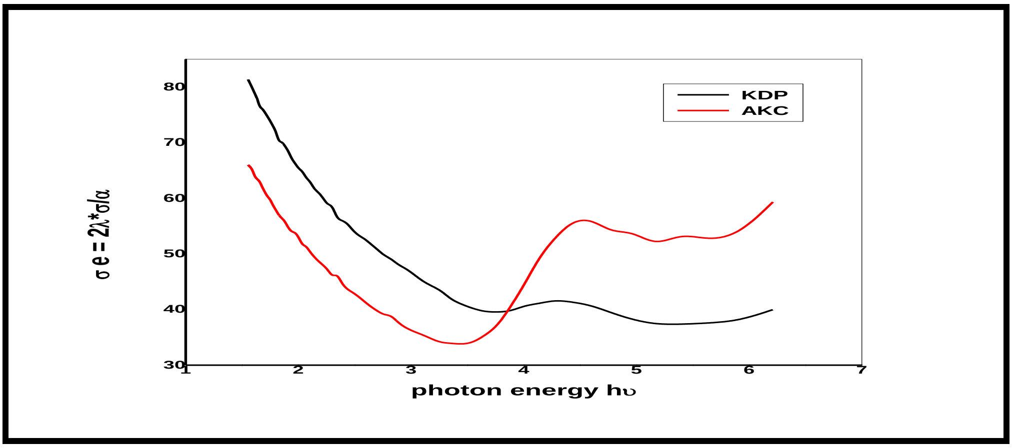

Figure 10: Electrical susceptibility Vs Photon Energy

X-Ray Diffractometer (XRD)

Table 1: X-Ray Diffractometer (XRD)

Crystal	a (Å)	b (Å)	c (Å)	V (Å)^3	Structure	Space group
KDP	7.441	7.441	6.942	384.36	Tetragonal	I-4d
Acetic acid doped KDP	7.443	7.443	6.953	385.18	Tetragonal	I-4d

Using single crystal XRD, one may determine the features and structure of the crystal. An EnfradNoniu CADA-MV31 X-ray diffractometer was used to perform single crystal X-ray diffraction on pure KDP and acetic acid doped KDP crystals [4,5]. It has been established that the crystal belongs to the tetragonal system, and table no. 1 discusses the values of the lattice parameters. There was a small increase in the cell volume of the KDP crystals treated with acetic acid as the amount of acetic acid increased. While the space class and crystal structure stay the same, the addition of dopants also improves the volumetric characteristics of the formed crystals [6,7].

Second Hormone Generation (SHG)

Table 2: Second Hormone Generation (SHG)

Crystal	SHG efficiency
KDP	1
Acetic acid doped KDP	1.39

1Using Kurtz's powder approach, it was possible to examine how the addition of1 mole of acetic acid to KDP crystal increased its SHG efficiency. The study used a 10 Hz frequency rate and 0.74 mW input power Nd-YAG laser operating at 1064 nm. It was found that the estimation error bar using the current system was±1 mV. Green radiation emissions from the crystalline specimen were used to demonstrate the production of second harmonic signals. One mole of added acetic acid increases the SHG's effectiveness by introducing KDP crystal. It turns out that the value is 1.39 times larger than the typical KDP material. The crystalline sample's frequency doubling phenomenon has been determined. As a result, KDP crystal with acetic acid added can be used for NLO applications such optical modulation and efficient laser frequency conversion [8-10]. As acetic acid concentration rises to 1% mole, there is a noticeable improvement in KDP's SHG efficiency.

photolumince

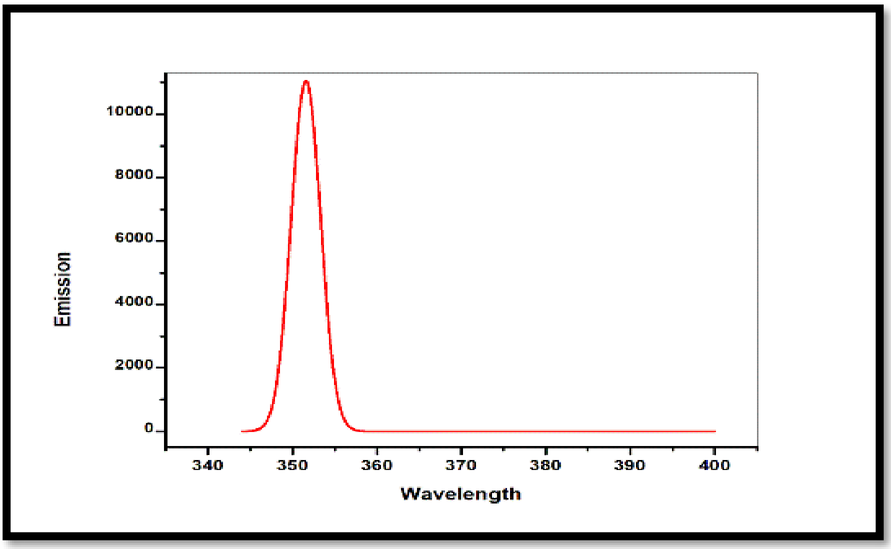

Figure 11: Photolumince (Emission Vs Wavelength)

The emission spectrum of photo-excited materials provides valuable insights into intrinsic impurities, electronic transition states, and surface characteristics. Photoluminescence (PL) intensity is influenced by both the excitation energy and the incident beam’s intensity. In this study, the AKC crystal was photoexcited using a wavelength of 358 nm (about 3.58 eV) and the emission spectrum was captured between 340 and 400 nm using an F-7000 FL spectrophotometer (with a response time of 0.1 s, an EM slit width of 1 nm, and a scan speed of 240 nm/min).The resulting emission spectrum as above reveals strong violet emission from the acetic acid doped crystal, with prominent peaks centered at 36 nm. This peak corresponds to energies of 3.58 eV. The distinct Photoluminescence features indicate that the AKC crystal possesses excellent optical quality—a crucial requirement for materials to exhibit nonlinear optical (NLO) behavior. Given its pronounced violet emission, the AKC crystal could serve serving as a valuable reference material for element detection in various fields, including biotechnology, chemistry, and medicine.

4. Conclusion

This study systematically investigated the impact of 1M acetic acid doping on the optical, structural, and nonlinear optical properties of potassium dihydrogen phosphate (KDP) single crystals grown using the slow evaporation solution technique. UV–Visible spectral analysis revealed a significant improvement in optical transparency, with doped KDP crystals exhibiting a transmittance of 80% compared to 60% for undoped crystals. This enhanced transparency is highly desirable for optoelectronic applications, particularly in devices utilizing second harmonic generation (SHG) and laser frequency conversion systems. Additionally, the optical band gap increased from 5 eV in pure KDP to 5.3 eV in acetic acid-doped crystals, indicating reduced defect density and improved crystal quality. Photoluminescence analysis demonstrated a strong violet emission peak at 358 nm, corresponding to energy of 3.58 eV. This emission indicates minimal impurities and superior optical homogeneity in doped crystals, making them suitable for NLO applications and optical modulation devices. Furthermore, the SHG efficiency of the doped crystals increased by 1.39 times compared to pure KDP crystals, validating their enhanced nonlinear optical performance.

The structural analysis using X-ray diffraction (XRD) confirmed that both pure and doped KDP crystals possess a tetragonal crystal system, with slight increases in lattice parameters and cell volume after doping. This indicates that the incorporation of acetic acid modifies the crystal lattice without disrupting its fundamental structure, contributing to improved optical properties. Additionally, the refractive index and reflectance of doped KDP crystals were notably lower than those of undoped crystals, highlighting their potential for anti-reflective coating applications in photonic devices. The observed optical uniformity and reduced defect formation further enhance the crystal's suitability for high-precision optical systems.

In conclusion, the incorporation of acetic acid into KDP crystals significantly enhances their optical transmittance, band gap, photoluminescence, and SHG efficiency while maintaining structural stability. These advancements underscore the potential of acetic acid-doped KDP crystals in advanced optoelectronic applications, including electro-optic modulators, laser frequency converters, and photonic devices. The findings emphasize the importance of organic dopants in tailoring the functional properties of nonlinear optical crystals, paving the way for their deployment in next-generation optical technologies.

Conflict of Interest: Declared None

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