RESEARCH ARTICLE

**Growth and Characterization of Pure and Metal Halides Doped Acetoacetanilide Single Crystals**

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**ABSTRACT**

The focus of this paper is on growing quality single crystals of pure acetoacetanilide and NaCl and KCl doped acetoacetanilide which possess better nonlinear optical properties. Solvent evaporation technique was used for growing these crystals. The solution and operation temperature used was ethanol and 30 °C respectively. Single crystal X-ray analysis was used to determine the grown crystals lattice parameters. The crystalline perfection was identified by the well-defined sharp peak in the pattern of powder X-ray diffraction. The presence of dopants and transparency of the doped crystals are confirmed by the ICP AES spectrum and the UV–Vis NIR spectral study respectively. This emphasizes the AA crystal host lattice of metal ion inclusion. The optical band gap of the pure AA, NaCl doped AA (AANC) and KCl doped (AAKC) crystals was found to be 5.09, 5.48 and 5.74 eV respectively. Kurtz powder technique assessed the second-order non-linearity of the grown crystal. The pure and doped AA second harmonic generation efficiency was projected to be larger than KDP by a factor of 4. The dielectric measurement reveals that there is a small dielectric constant and dielectric loss at greater frequencies for both the types of AA. Photo conducting nature was confirmed by the photocconductivity studies of pure and doped AA.

**Keywords:** Solution growth, Micro hardness, NLO, UV-Vis. Absorption, Dielectric, Photoconductivity.

**1. INTRODUCTION**

Nonlinear Optical (NLO) materials find their application in information processing as well as electro-optic switching elements. The NLO process needs resources which can alter the components of optical beams such as phase, amplitude, frequency and polarization. Organic, inorganic, organometallic and polymeric materials have been studied considering their NLO activity. Among them the organic materials have been assigned much importance since they possess many advantages regarding synthesis, response time, photo-stability and hyperpolarizability (β) values. π-conjugated systems linking a donor (D) and an acceptor (A) have been well studied due to their large NLO response.

Single crystal growth from aqueous solution is an area of interest as high-power laser technology and its applications are rapidly gaining interest. Study of this area of crystal growth and the respective in-depth examination of different key systems results in basic case studies generating the theory and technology applicable to the process of crystal growth from solutions. One of the significant advantages of solution growth is that it provides control over viscosity and temperature. In addition to it they are simple and have high degree of crystal perfection since the growth of the crystals is at a temperature very lower than their melting point.

Acetanilide and its derivatives exhibit analgesic activity and are of great significance in the medical field [1]. Acetoacetanilide [AA] (CH₃-CO-CH₂-CO-NH-C₆H₅) is one such derivative with excellent NLO properties. It finds its application in seed coatings and pigment production in the role of...
a chemical intermediate. Very few studies are being carried out for the growth and characterization of these crystals [2, 3, 4]. The effect of Swift Heavy Ion (SHI) irradiation on the dielectric properties of acetoacetanilide crystals have been reported in [5]. In practical applications, they possess certain limitations such as narrow transparency window and high optical absorption. In addition to it they possess negligent mechanical and thermal stability. They are doped to overcome these difficulties. Various modifications due to the addition of impurities are also taken into account.

Trace aggregates of impurities existent in the mother phase may result in changes in crystal properties, morphology and growth rates [6, 7, 8]. This paper discusses the growth of pure as well as NaCl and KCl (metal halide additives) added acetoacetanilide single crystals. Study on the effects of additives on the physico-chemical characteristics of acetoacetanilide crystals was also carried out.

2. EXPERIMENTAL

2.1. Growth aspects

Acetoacetanilide was exposed to various processes of recrystallization. Ethanol was taken as the charge material for crystal growth. The saturated solutions of acetoacetanilide [AA], NaCl (0.02 M) doped acetoacetanilide [AANC] and KCl (0.02 M) doped acetoacetanilide [AAKC] were first prepared in a solution of ethanol at 30 °C. The solution was filtered using Whatman filter paper (Grade 41). The filtered solution was set in three glass beakers and exposed to controlled evaporation of the solvent at 30°C. This was facilitated by a constant temperature bath setup. Spontaneous nucleation method was used to develop seed crystals which are optically transparent and fault free. For bulk growth, the selected seed crystals were used (good plate like crystals were harvested in a five day span). We have successfully grown large size single crystals of pure AA (30x24x3.5 mm³), AANC (23x21x2 mm³) and AAKC (34x13x2.5 mm³) over a period of about 20-22 days and is depicted in figure B1. The results indicate that the doped crystals i.e. AANC and AAKC are as transparent as AA. This suggests that the advanced synthesis/doping procedure used in the current study did not result in any unwanted impurities in the crystal lattice/surface. Direct vision method was used to estimate the induction period (τ) upon the growth of our single crystal [9, 10, 11, 12]. We perceived that the nucleation rates of doped AA crystals are greater than that of pure AA crystals.

2.2. Solubility

For consideration as solvents for growing crystals, the solvents should possess moderate solubility-temperature gradient and a prismatic growth habit. Several trials were performed and it was observed that ethanol solution generated transparent crystals of acetoacetanilide. The crystal solubility was measured for four different temperatures viz., 30, 35, 40 and 45 °C. The solubility at a specific temperature was determined by dissolving the crystals in a solution of 100 ml ethanol in an airtight container. The temperature was maintained at the experimental temperature along with continuous stirring. After achieving saturation, the solute equilibrium concentration was gravimetrically estimated. Doped crystals were subjected to the same procedure. Figure B2 shows the temperature dependent solubility of pure and doped crystals. The solubility curve portrayed a positive solubility – temperature gradient so that the ethanol solution is appropriate for the bulk growth of the crystals. The solubility graph also displays that the solubility of pure AA, NaCl and KCl doped AA crystals rises with increase in temperature. However solubility is reduced for NaCl and KCl doped samples when compared to the pure one.

Prediction of the effect of impurities on crystal solubility, subsequently leads to changes in crystal growth rates. It can be deduced that the effects of changing solubility associated with impurity addition supports changes caused by kinetic and thermodynamic parameters. The influence of impurities on solubility is usually lesser at lower concentrations [13].

2.3. Characterization techniques

The grown AA, AANC and AAKC single crystals were subjected to single crystal X-ray diffraction studies using ENRAF NONIUS CAD-4 X-ray diffractometer with MoKα (λ=0.71069 Å) radiation. This was done to calculate the lattice parameter value. Powder X-ray diffraction analysis has been done using BRUKER AXS D8 Advance model diffractometer using CuKα1 (1.54560Å)
radiation. The FTIR spectra were found to be in the 400–4000 cm\(^{-1}\) range. Thermo-Nicolet Avatar 370 model spectrophotometer was used by the KB pellet method for studying the various functional group presences. Varian Cary 5000 UV-Vis-NIR spectrophotometer was used to study the linear optical properties of the crystals. The grown crystals have been subjected to the modified Kurtz powder SHG test for confirming the nonlinear optical property [14]. Shimadzu HMV 2000 Vickers micro hardness tester fitted with a Vickers diamond pyramidal indenter attached to an incident light microscope was used to carry out the micro hardness studies. Dielectric studies of both types of AA crystals were done at room temperatures for frequencies ranging from 500 Hz to 3 MHz by HIOKI 3532 LCR HITESTER. Photoconductivity studies were carried out at room temperature by using Keithley 485 picoammeter.

3. RESULTS AND DISCUSSION

3.1. Structural analysis
The unit cell dimensions and morphology was determined by exposing the grown crystals to single crystal X-ray diffraction studies. The crystallization of crystals occurred in the orthorhombic system. They come under the non-centro symmetric \(P2_12_12_1\) space group. This satisfies the basic criteria for the crystal SHG activity. The doped AA and pure AA doped parameters differ slightly. This is due to the Na\(^+\) and K\(^+\) ions in AA crystals. Table A1 presents the crystal data for both types of crystals. The dopants had negligible effect on the basic structure of AA crystals. The crystals were then powdered and subjected to X-ray diffraction studies in the range 5-50°. Figure B3 shows the X-ray powder diffraction patterns of the three types of crystals. The XRD peaks were indexed using UNIT CELL software package. The grown crystals exhibited orthorhombic symmetry. Structural parameters and JCPDS data (JCPDS file No. 09-0675) comparison of AA crystals reveals their orthorhombic structure. These values were in close agreement with the reported values [2, 4]. Table A2 shows the list of calculated lattice parameters.

The lattice parameter variation of the doped samples is a result of the addition of dopants in the AA crystal lattice. To support this, the best Gaussian fitted profile comparison for \(1 0 0\) peak was made. It is shown in figure B3. As noted, a change in the peak position and FWHM occurred due to dopant incorporation.

Floatation technique was used for density measurements. This was done using a liquid mixture of bromoform (density: 2.89 g/cc) and xylene (density: 0.89 g/cc). The AA crystal density was found to be 1.27 ± 0.01 g/cc. The obtained values and the reported values were in good agreement [4]. The grown crystal density was also calculated from the crystallographic data. The calculated density values of AA, AANC and AAKC crystals are 1.267 g/cc, 1.30 g/cc and 1.33 g/cc respectively.

The sodium and potassium presence in the doped AA crystals has been confirmed by ICP AES analysis using an Inductively Coupled Plasma Atomic Emission spectrometer (ICP-AES Thermo electron IRIS Intrepid II XSP DUO model). The analysis revealed that Na and K concentration is about 198.6 ppm and 165.2 ppm respectively in the acetoacetanilide crystals.

For analyzing the presence of functional groups and vibrational modes in AA, AANC and AAKC, Fourier Transform Infrared (FTIR) spectra have been recorded in the 400 cm\(^{-1}\) to 4000 cm\(^{-1}\) range. It is shown in figure B4. Table A2 shows the vibrational frequency of different functional groups of the grown crystals and their tentative assignments. The recorded FTIR spectrum for doped crystals was similar to those of pure AA crystals. This confirms existence of all functional groups. The replacement of metal dopants results in shifting and broadening of bands. This indicates the presence of dopants in AA crystals.

3.2. Micro hardness analysis
Mechanical strength of materials has a major role in device fabrication [15]. The chemical forces in a crystal resist the motion of dislocations because it involves displacement of atoms. This resistance is the intrinsic hardness of a crystal. Crystal hardness can be correlated with elastic constant, strength of interatomic bonding, yield strength compressibility etc. Vickers’s hardness is significant in cutting, grinding and polishing of bulk crystals in fabrication of device. Our study was conducted at the indentation plane of \(1 0 0\). The applied load was altered from 5 to 30 g with an indentation time of 10 seconds.


\frac{P}{d^2} \text{ Kg/mm}^2 \quad (3.1)

where \( H_v \) = Vickers micro hardness number
\( P \) = Indenter load (g)
\( d \) = the diagonal length of the impression (mm).

Diagonal lengths corresponding to the indented impressions at different loads were measured. Several indentations were made for each load. The mean value of the diagonal length (d) was used for the calculation of micro hardness. The differences of Vicker’s micro hardness values with load are shown in figure B5(a). The hardness increases with the increase in load and saturates when it exceeds 25 g. After 30 g, cracks began to develop on the surface of the crystals. The cause is the internal stress release by indentation. It indicates the Reverse Indentation Size Effect (RISE) [16]. The relation between the load and diagonal length is given by Meyer’s law as shown in (3.2) [17].

\[ P = Ad^n \]

where \( A \) = Material’s constant
\( n \) = Meyer’s index.

The grown crystal work hardening coefficient (n) for the (1 0 0) plane is found to be 2.131, 2.173 and 2.246 for pure AA, AANC and AAKC crystals respectively. This is calculated by taking a slope in the straight line of the graph between log d and log P. It is depicted in figure B5(b), n should be between 1 and 1.6 for hard materials and above 1.6 for softer ones [18]. This means that the observed values of n belong to soft materials category.

3.3. Linear and nonlinear optical analysis

The optical transmittance and absorption spectra of the grown crystals were taken in the range 190-1100 nm and are shown in figure B6. As displayed by the spectrum, the pure and doped samples are optically transparent over a wide wavelength region. The transmission percentage is high in the visible part of the UV region. The lower cutoff wavelength of AA is 244 nm. The dopant addition in the host AA lattice is shifted to 226 nm and 216 nm for AANC and AAKC crystals. The dopants improve the transmission percentage of doped crystals. The transmission of the grown crystals in the visible region is better confirming the colour less nature of the crystals. The absorbance is almost zero in the entire visible region and short cutoff wavelength makes it to be a potential NLO material for second and third harmonic of Nd:YAG laser. The plot of variation of \((\omega h \nu)^2\) and \(h \nu\) is shown in figure B6. \(\varepsilon_p\) is evaluated by the extrapolation of the linear part [19]. The band gap is found to be 5.09, 5.48 and 5.74 eV for pure AA, AANC and AAKC crystals respectively which indicates the higher energy band gap property of both type of materials.

Modifed Kurtz and Perry powder technique was used to measure the SHG intensity. The crystals were then powdered to uniform particle size in an uniform bore micro capillary tube. The samples were then exposed to the output of a Q-switched Nd:YAG laser which emits a fundamental wavelength of 1064 nm, 10 Hz repetition rate, 8 ns pulse width and an input power of 6.4 mJ. SHG confirmation was done by green radiation emission. A powdered potassium dihydrogen phosphate (KDP) sample, was used as the reference material in the present measurement. The signal amplitude in the oscilloscope denotes the grown crystal SHG efficiency. The sample KDP has been used as the reference material. The output power intensity of pure AA, AANC and AAKC has been found to be 4, 5.2 and 4.5 times respectively to that of the output power intensity of KDP. Results indicate that the frequency doubling efficiency in pure and doped AA crystals is better than the standard reference KDP crystal. In addition to it the doped AA crystal SHG efficiency is better than pure AA crystal.

3.4. Dielectric studies

Dielectric studies of both pure and doped AA crystals have been carried out at different operating temperatures and frequencies. The crystal behaviour in an electric field has a close relationship with the laser light irradiation. This enables the study of the power dissipation factor. The pure and doped AA crystal sample was coated with electrodes on both sides with an air drying silver paste forming a parallel plate capacitor. The sample capacitance was measured by varying the frequency from 500 Hz to 3 MHz at room temperature. Figure B7 shows plots dielectric constant \((\varepsilon_r)\) and dielectric loss factor \((\tan\delta)\) versus applied frequency.
studies deliver much information regarding the polarization induced dielectric constant developed in the material due to electric field variations. The literature specifies that the main effect is because of space charge polarization. More study is needed to on the system understanding [20, 21]. Considering Miller rule, the lower value of dielectric constant at higher frequencies is an appropriate parameter for SHG coefficient enhancement [22]. The metal ion doped AA crystal possess low dielectric constant compared to pure AA crystals owing to high molecular polarizability of Na⁺ and K⁺ ions. At a fixed frequency, the dielectric constant and dielectric loss is in the following hierarchical order viz AANC < AAKC < AA. This suggests that doped AA crystals are more preferred than AA for NLO applications. The low value of dielectric loss at higher frequencies implies good optical quality which is the required property of the materials to be used for different NLO applications, optical and communication devices etc., [23].

3.5. Photoconductivity studies

Keithley 485 picoammmeter was used for studying photoconductivity of single crystals. The studies were carried out at room temperature for both the type of crystals. Study on the dark conductivity of the sample was done by a series connection of the sample, Pico ammeter and DC power supply. Silver paint was used to make the electrical contact. The spacing was kept at 1.5 mm. The DC input was increased from 100 to 1500 V in steps of 100 V and the respective dark currents (I₀) were observed. Next the photo current (Iₚ) was measured. The sample was illuminated with a halogen lamp (100 W) by focusing a spot of light on the sample with a convex lens. The DC input was increased and the respective photocurrents were measured. Figure B8 shows the variations of photocurrent (Iₚ) and dark current (I₀) with applied field. The photo and dark current of crystals increases linearly with applied voltage. The crystal photocurrent is more than its dark current, which is known as positive photoconductivity [24, 25]. Generation of mobile charge carriers and absorption of photons are the main reasons for it. The photocurrent of doped samples was also found to be greater than pure AA.

4. CONCLUSION

Single crystals of pure, NaCl and KCl doped acetoacetanilide are grown using ethanol as a solvent by the slow evaporation method at 30 °C over three weeks. Orthorhombic structures of the grown crystals were confirmed by the single crystal XRD studies. Variations in the relative intensities, lattice parameters and peak positions confirm the metallic dopants existence in AA crystals. ICP AES analysis quantifies the concentration of dopants. The hardness of the AA crystals was slightly improved by the incorporation of dopants. The lower cutoff wavelength of pure and doped AA at recommends this material as a potential candidate for frequency doubling. The powder SHG analysis reveals that the efficiency of these materials is greater than that of KDP by a factor 4. Dielectric studies confirm that the dopants have slightly changed the dielectric nature of AA crystals. Photoconductivity studies show that the dark current value was lesser than the photocurrent value exhibiting positive conductivity. Thus doped crystals are a promising material for nonlinear optical applications and fabrication of electro-optic devices.

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### APPENDIX A

Table A1. Obtained lattice parameter values of pure and metal ions doped acetoacetanilide single crystals from single crystal and powder XRD data.

| Crystal parameters | Single crystal XRD data | Powder XRD data |
|-------------------|-------------------------|-----------------|
|                   | Pure AA | AANC | AAKC | Pure AA | AANC | AAKC |
| a (Å)             | 11.0752 | 11.0863 | 11.0929 | 11.0842 | 11.0921 | 11.1021 |
| b (Å)             | 19.2827 | 19.2947 | 19.3124 | 19.2775 | 19.2965 | 19.3386 |
| c (Å)             | 8.6882  | 8.7035 | 8.7171 | 8.6912  | 8.7107 | 8.7018 |
| V (Å³)            | 1855.93 | 1861.73 | 1867.46 | 1857.09 | 1864.42 | 1868.27 |
| α = β = γ         | 90°     | 90°   | 90°   | 90°     | 90°   | 90°   |
| System            | Orthorhombic | Orthorhombic |
| Space group       | P2₁₂₁₂₁ | P2₁₂₁₂₁ | P2₁₂₁₂₁ | P2₁₂₁₂₁ | P2₁₂₁₂₁ | P2₁₂₁₂₁ |

Table A2. FTIR assignments of pure and metal halides doped AA single crystals

| Pure AA (cm⁻¹) | AANC (cm⁻¹) | AAKC (cm⁻¹) | Assignments                        |
|----------------|-------------|-------------|------------------------------------|
| 3068.26        | 3080.25     | 3076.42     | Aromatic CH-stretching              |
| 2952.65        | 2963.11     | 2957.11     | Asymmetric and symmetric stretching modes CH₃ and CH₂ group. |
| 2923.89        | 2932.68     | 2929.26     |                                      |
| 1725.79        | 1730.21     | 1728.61     | keto C=O and anilide C=O groups      |
| 1661.00        | 1671.12     | 1668.43     | keto C=O and anilide C=O groups      |
| 1599.09        | 1605.11     | 1602.31     | Aromatic ring vibrations            |
| 1498.22        | 1507.32     | 1504.11     | Aromatic ring vibrations            |
| 1445.93        | 1451.27     | 1450.17     | Aromatic ring vibrations            |
| 1541.29        | 1548.21     | 1545.22     | CN stretching                       |
| 1445.93        | 1451.27     | 1450.17     | CH₂ -bending modes                  |
| 1341.27        | -           | 1344.10     | CH₂ -bending modes                  |
| 756.08         | 760.85      | 763.21      | Confirm the aromatic ring is mono substituted |
| 691.34         | 697.32      | 695.22      |                                      |

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APPENDIX B

Figure B1. Photograph of the (a) pure acetoacetanilide [AA] (b) 0.02 M of NaCl doped acetoacetanilide [AANC] (c) 0.02 M of KCl doped acetoacetanilide [AAKC] single crystals (d) crystal orientation of AA crystal [2].

Figure B2. Solubility curve of pure and metal halides doped AA single crystals in ethanol solution.
Figure B3. Indexed powder XRD pattern of pure and metal halides doped AA single crystals. The FWHM values measured for AA, AANC and AAKC, respectively, 0.1186, 0.1223 and 0.0963.

Figure B4. FTIR spectrum of pure and metal halides doped AA single crystals.
Figure B5.(a) Variation of Vickers hardness number with applied load (b) plots of log d vs. log p for pure and metal halides doped AA single crystals.
Figure B6. Optical absorption spectrum of pure and doped AA single crystals. The inset shows the determination of optical band gap energies for the respective samples.
Figure B7. Frequency dependence of electrical parameters such as (a) dielectric constant $\varepsilon_r$ (b) dielectric loss factor $\tan\delta$ for the frequency range of 500 Hz to 3 MHz at a constant temperature (30 °C).
Figure B8. Field-dependent dark and photo conductivity of pure AA, AANC and AAKC single crystals.