5. GROWTH AND CHARACTERIZATION OF POTASSIUM DICHROMATE (KDC) SINGLE CRYSTAL

5.1 INTRODUCTION

In recent years, the nonlinear optical materials are attracted by researchers owing to their application to high-speed all-optical switching devices [135]. The search for large third order optical nonlinearities and fast response is essential for technological development in nonlinear optical materials [72]. The nonlinear optical processes provide the significant functions of frequency of the system. The applications depend upon the various properties of the materials, such as transparency, birefringence, laser damage threshold, refractive index, dielectric constant, second order nonlinearity, large third order susceptibilities, etc. Nonlinear optical materials with large third order nonlinear susceptibilities are essential for all-optical switching, modulating and computing devices because the magnitude of this quantity dominates the device performance [136-139]. The introduction of the Z-scan technique [81] for the determination of third order optical nonlinearities brought a flood of activity to the field of third order nonlinear optical (NLO) materials. The achievement of the technique and the analysis of the results being rather simple, the Z-scan were used in numerous NLO investigations [119]. V. Natarajan et al has reported third order nonlinear optical properties in Centro-symmetry nature potassium aluminium sulphate single crystal using Z-scan technique [140]. The third order nonlinear optical (NLO) materials with weak nonlinear absorption (NLA) but strong nonlinear refraction (NLR) has attracted considerable attention because of their potential uses in the optical signal processing devices [141,142]. The Z-scan technique is a popular method to measure the optical nonlinearity of a given material. It has the advantage of high sensitivity and simplicity. [67,143]. One could simultaneously measure the magnitude and sign of the nonlinear refraction and nonlinear absorption, which are associated with the real part \( \text{Re } \chi^{(3)} \) and imaginary part \( \text{Im } \chi^{(3)} \) of the third order nonlinear susceptibilities.
5.2 CRYSTAL GROWTH

The potassium dichromate (KDC) crystals were grown by solution growth technique. AR grade potassium dichromate was dissolved in double distilled water and stirred well for 6 hours at room temperature. The purity of the salt was increased by recrystallization process. The saturated solution was filtered through Whatmann filter paper then it was closed with a perforated cover and kept in a dust free atmosphere. The seed crystals were harvested in a time period of 22 days. Optically transparent and defect-free crystal were having dimensions $15 \times 8 \times 5 \text{ mm}^3$ was grown and the photograph of the grown crystal is shown in Figure 5.1.

![Figure 5.1: As grown single crystal of KDC.](image)

5.3 RESULTS AND DISCUSSION

5.3.1 Single crystal and powder X-ray diffraction studies

Well shaped, transparent and quality single crystal of potassium dichromate crystal was selected and it was subjected to single crystal XRD analysis at room temperature. It was carried out using a Bruker AXS diffractometer with MoK$_\alpha$ ($\lambda = 0.7170$ Å) radiation to identify the lattice parameters. The intensity data were collected up and accurate unit cell parameters were obtained based on all reflections. From the single crystal X-ray diffraction study, it is revealed that the KDC crystal belongs to the triclinic
system with space group $P\bar{1}$. The lattice parameters obtained as, $a = 7.38 \text{ Å}$, $b = 7.46 \text{ Å}$, $c = 13.38 \text{ Å}$, $\alpha = 95.19^\circ$, $\beta = 98.06^\circ$, $\gamma = 90.93^\circ$ and the volume of the unit cell is found to be $= 724.0 \text{ Å}^3$.

The powder XRD study was carried out using a Rich–Seifert diffractometer with CuK$\alpha$ ($\lambda = 1.5406$ Å) radiation. The indexed powder XRD pattern of the grown KDC crystal as shown in Figure 5.2. The powdered KDC sample was scanned over the range 10- 40° at the rate of 1° per min. Sharp and strong peaks confirmed the good crystallinity of the grown crystal. From the powder X-ray data, the various planes of reflections were indexed using XRDA 3.1 program. The lattice parameters are evaluated as: $a = 7.42\text{Å}$, $b = 7.40 \text{ Å}$, $c = 13.40 \text{ Å}$, $\alpha = 96.17^\circ$, $\beta = 98^\circ$, $\gamma = 90.83^\circ$, and volume of the unit cell is $= 733.82 \text{ Å}^3$. The obtained lattice parameters from the powder XRD analysis are in good agreement with the literature reported values and single crystal XRD analysis [144]. The structural data for KDC single crystal and powder X-ray data are listed in table 5.1.

![Figure 5.2: Powder X-ray diffraction spectrum of KDC crystal.](image)
Table 5.1 Structural data for KDC single crystal

<table>
<thead>
<tr>
<th>Lattice parameters</th>
<th>Single crystal XRD value</th>
<th>Powder XRD value</th>
<th>Reported value [144]</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å)</td>
<td>7.38</td>
<td>7.42</td>
<td>7.37</td>
</tr>
<tr>
<td>b (Å)</td>
<td>7.46</td>
<td>7.40</td>
<td>7.44</td>
</tr>
<tr>
<td>c (Å)</td>
<td>13.38</td>
<td>13.40</td>
<td>13.36</td>
</tr>
<tr>
<td>α</td>
<td>95.19</td>
<td>96.17</td>
<td>96.21</td>
</tr>
<tr>
<td>β</td>
<td>98.06</td>
<td>98.0</td>
<td>97.96</td>
</tr>
<tr>
<td>γ</td>
<td>90.93</td>
<td>90.83</td>
<td>90.75</td>
</tr>
<tr>
<td>Volume</td>
<td>724.0</td>
<td>733.82</td>
<td>722.3</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Triclinic</td>
<td>Triclinic</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P̅1</td>
<td>P̅1</td>
<td>P̅1</td>
</tr>
</tbody>
</table>

5.3.2 Optical absorption study

The optical absorption spectrum of the grown crystal was recorded in the wavelength range between 200 and 800 nm using Perkin-Elmer lamda 25 UV-Spectrometer and the resultant spectrum is shown in Figure 5.3. The crystal is transparent in the entire visible region and the UV cut-off wavelength is found as 240 nm. The very low absorption in the entire visible region confirms its suitability for the fabrication of nonlinear optical devices [145].
5.3.3 Thermal analysis

TGA and DTA analysis of KDC crystal were carried out with the help of TG/DTA 6200 SII EXSTAR 6000 (Figure 5.4) using alumina as reference. A sample of weight 3.84 mg was taken in a crucible. The sample was heated at a rate of 20°C/min in the nitrogen atmosphere. Both the TGA and DTA curves show that the melting point of KDC is 400 °C. The TGA curve shows that the material has high thermal stability; it is stable up to 397.1°C. The TGA curve shows that the major decomposition takes place after 700°C. The DTA line shows two endothermic peaks 277.5 °C and 400 °C. Around 99.4% of the material decomposes at 800°C.
5.3.4 Mechanical study

Vicker’s microhardness study was carried out using REICHERT POLYVAR 2 hardness test attached with Micro-Duromat4000E. The hardness of the material depends on different parameters, such as lattice energy, Debye temperature heat of formation and inter atomic distance [146, 147]. According to Gong [148], during an indentation process, the external work applied by the indenter is converted to a strain energy component to the volume of the resultant impression and the surface energy component proportional to the area of the resultant impression. The applied loads were 10 g to 60 g and hardness numbers calculated using the relation [149].

\[
H_v = \frac{1.8554P}{d^2} \text{ kg / mm}^2
\]  

\[ (5.1) \]

\( H_v \) - Vicker’s micro hardness number, \( P \): applied load (g), \( d \): diagonal length (mm) of the indentation. The microhardness value was taken as the average of the several impressions made. Crack initiation and materials chipping become significant beyond 58 g of the applied load (Figure 5.5).
Chemical etching study was carried out using high magnification REICHERT POLYVAR 2 MET microscope. Etching studies were carried out to study the growth mechanism and assess the perfection of the growth crystal. Etching is the selective dislocation of the crystal surface, which reveals the growth mechanism and surface features. In the present work, etching study was carried out on KDC crystal using deionized water as an etchant. The reactants which are absorbed more strongly produce better contrasting pits. Etching was carried out for 10 s and 30 s. The etched surface was dried by pressing gently between filter papers. Optical microscope pictures were taken which are shown in the Figure 5.6 (a) and (b). Well defined pyramidal etch pits were formed on the surface of the grown crystal. This is an indicator of two-dimensional layer growth mechanisms due to the presence of growth hillocks in association with striations.
Figure. 5.6: Photograph of the etching pattern for (a) 10s, (b) 30s.

5.4 NONLINEAR OPTICAL (NLO) STUDIES

5.4.1 Second Harmonic Generation (SHG) Study

Powder SHG study for KDC single crystal was carried out in accordance with the classical powder method developed by Kurtz and Perry method [129]. A Q-switched Nd: YAG laser (\( \lambda = 1064 \) nm, Quanta Ray, USA) beam of wavelength 1064 nm and pulse with of 6 ns with a repetition rate of 10 Hz was used. The potassium dichromate powder placed in a micro capillary was exposed to laser radiation. The second harmonic signal was absent for this sample and it confirms the Centro-symmetric nature of the crystal.

5.4.2 Z-scan study

Z-scan technique [61,81] based on the spatial distortion of a laser beam, passed through a nonlinear optical material, is widely used in material characterization because of their simplicity, high sensitivity and well-elaborated theory. The saturation absorption for the sample in solvent at a transmission of about 50% . The closed aperture Z-scan curve of potassium dichromate (KDC) crystal as shown in Figure.5.7.(a). The peak followed by a valley-normalized transmittance curve obtained from the closed aperture Z-scan data, indicates that the sign of the refraction nonlinearity is negative i.e. self-defocusing nature [150]. As the material has a negative refractive
index it results in defocusing nature of the material, which is an essential property for the application in the protection of night vision devices [151]. The open aperture Z-scan curve is shown in Figure 5.7 (b). Therefore, it is necessary to separate the effect of nonlinear refraction from that of the nonlinear absorption. Represents such plots obtained for the samples, i.e., the ratio of closed aperture and the open aperture Z-scan as shown in Figure 5.7 (c). The data obtained in this way reflects purely the effects of nonlinear refraction.

The nonlinear parameters, such as nonlinear refractive index $n_2$, nonlinear absorption coefficient $\beta$, and nonlinear susceptibility $\chi$, values of potassium dichromate (KDC) crystal were calculated similarly to the discussed in chapter 4 and the values are presented in table 5.2.

**Table 5.2 Nonlinear optical parameters of KDC single crystal**

<table>
<thead>
<tr>
<th>Compound</th>
<th>$n_2 \times 10^{-8}$ (cm$^2$/W)</th>
<th>$\beta \times 10^{-4}$ (cm/W)</th>
<th>$\chi^{(3)} \times 10^{-6}$ esu</th>
</tr>
</thead>
<tbody>
<tr>
<td>KDC</td>
<td>9.41</td>
<td>0.57</td>
<td>4.68</td>
</tr>
</tbody>
</table>
Figure 5.7: (a) Closed aperture Z-scan curve for KDC crystal (b) Open aperture curve for KDC crystal, (c) Ratio curve of KDC crystal.
5.5 CONCLUSION

The single crystal of potassium dichromate (KDC) was successfully grown from an aqueous solution using slow evaporation technique. The single crystal X-ray and Powder X-ray diffraction studies confirm the triclinic structure with space group \( P\overline{1} \). The UV cut off wavelength is found occur at 240 nm. TG-DTA studies revealed that the crystal is thermally stable up to 397.1°C. The mechanical and etching studies of the grown crystal was carried out. The absence of second harmonic generation material confirms the centro symmetric nature of the grown crystal. Closed aperture Z-scan study reveals the negative nonlinearity in the crystal and open aperture Z-scan study confirms the saturation absorption. The nonlinear parameters values were evaluated. The third order nonlinear properties confirm its suitability of KDC crystals for nonlinear optical devices, such as optical limiting and optical switching.