THERMAL AND OPTICAL PROPERTIES OF PHTHALATE BASED NLO CRYSTALS- A COMPARATIVE STUDY

R. MURALIEMDHARAN 1, J. RAMAJOTHI2, G. VINITHA3
1* Department of Physics, PRIST Deemed University, Thanjavur
2 Department of Physics, Anna University, Chennai
3 School of Advanced Sciences, VIT Chennai,
Chennai*Corresponding author: jrramajothi@annauniv.edu

ABSTRACT

The potassium acid phthalate (KAP), sodium acid phthalate (SAP) and ammonia acid phthalate (AAP) single crystals were grown by evaporation technique. Single crystal XRD and FTIR analysis are used to evaluate the unit cell parameters and functional groups, respectively. UV-Vis spectral experiments are used to investigate the optical properties of the crystals. The crystals' thermal stability was calculated using TG/DTA analyses, and the microhardness was determined using Vicker's hardness test. The SHG efficiency and $\chi^3$ susceptibility was measured using Nd;YAG laser.

Keyword: Single crystalsXRD, Microhardness, TG/DTA, Nd;YAG laser.

I. INTRODUCTION

The semiorganic phthalic acid derivative crystals could be used in NLO and electro-optic processes [1-4]. Acid phthalate crystals are well-known for their use in long-wave X-ray spectrometers and as substrates for the deposition of thin films of organic nonlinear materials. [5-8]. The single crystals of KAP, SAP and AAP were grown by slow evaporation technique. The structure, thermal, mechanical, optical constant and $\chi^3$ susceptibility properties of KAP, SAP and AAP single crystals were discussed.

II. SYNTHESIS AND CRYSTAL GROWTH

Synthesis of SAP and AAP

The SAP salt was synthesized using sodium bicarbonate and phthalic acid in the equimolar ratio of 1:1 in water. The reaction that takes place between sodium bicarbonate and phthalic acid as follows

\[
\text{HO-} + \text{Na}^+ + \text{O}^- \rightarrow \text{Na}^+ \text{ HO-O-} \]

Similarly, AAP salt was synthesized by taking ammonia and phthalic acid in the equimolar ratio of 1:1 according to the following reaction
Growth of KAP, SAP and AAP Single Crystals

One mole of KAP was dissolved in the 150 ml of distilled water (pH = 4.2) then allowed for crystallization. After three weeks, a clear transparent regular shape good quality KAP single crystal with size of $28 \times 37 \times 6$ mm$^3$ have been harvested (Fig. 1 (a)).

The solution of SAP was prepared at pH = 3.8, then the solution were allowed for crystallization. The good quality well defined single crystal with a size of $17 \times 10 \times 3$ mm$^3$ was obtained within 27 days (Fig. 2 (a)). Similarly, SAP solution was prepared at pH = 4.6 and the solution were allowed for crystallization at room temperature. The single crystals of size $25 \times 17 \times 10$ mm$^3$ were cultivated in the period of 25 days (Fig. 3 (a)). The transparency of the SAP was improved by repeated recrystallization processes and grown crystal with well-developed planes with size is $20 \times 20 \times 25$ mm$^3$ is shown in Fig. 4. The AAP salt was dissolved in distilled water and the good quality single crystal with a size of $8 \times 10 \times 5$ mm$^3$ was harvested within a 28 days (Fig. 5 (a)).
Fig. 3 (a) Single crystal of SAP (pH = 4.6), Fig. 3 (b) Morphology of SAP (pH = 4.6).

Fig. 4 Single crystal of SAP.

Fig. 5 (a) Single crystal of AAP, Fig. 5 (b) Morphology of AAP.

Experimental Techniques
III. SINGLE CRYSTAL XRD

From the XRD data, the KAP, SAP and AAP belongs to orthorhombic crystal system (Table. 1). The prominent planes are assigned in the morphology of KAP, SAP (pH = 3.8 & 4.6) and AAP are shown in Figs. 1 (b), 2 (b), 3 (b) and 5 (b) respectively. The effect of pH change in SAP morphology has been observed and there is no change in observed crystalline lattice.

Table 1. Cell parameters of KAP, SAP and AAP.

<table>
<thead>
<tr>
<th>Crystal</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>V (Å³)</th>
<th>α = β = γ</th>
<th>System</th>
</tr>
</thead>
<tbody>
<tr>
<td>KAP</td>
<td>9.853</td>
<td>13.545</td>
<td>6.784</td>
<td>905.385</td>
<td>90°</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>SAP</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(pH= 3.8)</td>
<td>6.805(8)</td>
<td>9.23(1)</td>
<td>26.19(1)</td>
<td>1645.55</td>
<td>90°</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>SAP</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(pH= 4.6)</td>
<td>6.7834</td>
<td>9.2904</td>
<td>26.3728</td>
<td>1661.9889</td>
<td>90°</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>AAP</td>
<td>6.4195</td>
<td>10.277</td>
<td>26.0331</td>
<td>1717.38</td>
<td>90°</td>
<td>Orthorhombic</td>
</tr>
</tbody>
</table>

IV. FTIR SPECTRUM

The FTIR spectrum of KAP, SAP and AAP was recorded using Perkin Elmer RXI spectroscopy (Fig. 6). The O-H stretching vibration was observed at 3469 cm⁻¹ of KAP was shifted to higher frequency of 3499 cm⁻¹ in SAP [6- 9]. The broad peak (~3250 cm⁻¹) in AAP is due to the combination of N-H and O-H stretching vibration [10, 11]. The peaks at 1563 cm⁻¹ and 1558 cm⁻¹ represent the presence of carboxlate ion in KAP and AAP respectively [6, 10]. The same vibration band was shifted to higher frequency of 1720 cm⁻¹. The peaks at 1285 cm⁻¹, 1348 cm⁻¹ and 1388 cm⁻¹ represent the presence of C-O stretching vibration of KAP, SAP and AAP respectively [6, 10, 13]. The C-H out of plane deformation was observed at 718 cm⁻¹, 753 cm⁻¹ and 718 cm⁻¹ in KAP, SAP and AAP respectively [6, 10, 12].

Fig. 6 FTIR spectrum of KAP, SAP and AAP.
V. UV-VIS SPECTRAL STUDIES

Using a UV-Vis Spectrophotometer, the transmittance spectrum of KAP (2 mm thickness), SAP (2 mm thickness), and AAP (2 mm thickness) was investigated (Fig. 7). The lower cut off wavelength for KAP and SAP is 300 nm whereas AAP has lower cutoff wavelength is 310 nm which is suitable for lasers application [14, 15].

![Fig. 7 UV-Vis transmittance spectrum.](image-url)

The direct band gap of KAP (Fig. 8) and SAP (Fig. 9) was found to be 4 eV whereas AAP (Fig. 10) has 3.8 eV using Tauc’s plot [16-18].

![Fig. 8Tauc’s plot of KAP crystal.](image-url)
The extinction coefficient of the crystals decreases with increasing photon energy (Fig. 11). The reflectance of KAP, SAP and AAP increases with increasing photon energy (Fig. 12).

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**Fig. 9** Tauc's plot of SAP crystal.

**Fig. 10** Tauc's plot of AAP crystal.

**Fig. 11** Extinction coefficient (k) Vs Photon energy.
VI. THERMAL ANALYZES

The TG/DTA of KAP (Fig. 13), SAP (Fig. 14), and AAP (Fig. 15) was carried out using SDT Q 6000 analyzes. According to the TGA curve, the KAP has excellent thermal stability up to 292°C, with no weight loss below that temperature. Due to the liberation of volatile substances in the compound, the main weight loss of 45 percent occurred in the temperature range 292-300°C on the TGA curve. The DTA curve shows that the melting point of KAP is 297°C, and this melting point value is well agreed with melting point measured using conventional method. The material undergoes endothermic transition around 308°C followed by another endothermic peak at 440°C. The TG curve of SAP shows that weight loss about 40% due to the liberation of sodium and carbon monoxide. In DTA curve the first endothermic peak at 120°C which indicates the loss of water molecule and followed by the second endothermic peak at 211°C which can be assigned to the melting point of the sample. The AAP TG curves indicate that ammonia liberation causes a 60% weight loss in the temperature ranges of 172-194°C. From DTA curve, the melting point of the AAP is 185°C.

Fig. 13 TG-DTA curves of KAP.
VII. VICKER’S MICROHARDNESS MEASUREMENT

The hardness were performed with various load and the hardness increases with the increases of load (Fig. 16). The work hardening coefficient (Fig. 17) of KAP, SAP and AAP are found to be 3.23, 2.46 and 3.62 respectively which indicates all crystals belongs to soft material category.
VIII. MEASUREMENT OF SHG EFFICIENCY

The SHG efficiency of the KAP and SAP was found to be 0.4 and 1.1 times higher than that of the KDP, respectively. The AAP single crystal doesn’t exhibit SHG efficiency due to the centrosymmetric space group so we move the THG using Z-Scan technique.

IX. MEASUREMENT OF THG USING Z-SCANNING TECHNIQUE

The Z-scan experiments of KAP, SAP and AAP were carried out using Nd:YAG laser beam [19- 21]. The closed and open aperture of KAP, SAP and AAP are shown in Figs. 18 and 19 respectively. The ratio of open and close aperture of KAP, SAP and AAP is shown in Figs. 20. The nonlinear properties of KAP, SAP and AAP are shown in table 2.
Fig. 18 Closed aperture of KAP, SAP and AAP.

Fig. 19 Open aperture curve of KAP, SAP and AAP.
Fig. 20 Ratio of open and closed aperture of KAP, SAP and AAP.

Table 2 Nonlinear optical properties of KAP, SAP and AAP.

<table>
<thead>
<tr>
<th>Sample</th>
<th>KAP</th>
<th>SAP</th>
<th>AAP</th>
</tr>
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<tbody>
<tr>
<td>$n_2$</td>
<td>$3.13 \times 10^{-8}$ cm$^2$/W</td>
<td>$9.179 \times 10^{-8}$ cm$^2$/W</td>
<td>$9.164 \times 10^{-8}$ cm$^2$/W</td>
</tr>
<tr>
<td>$\beta$</td>
<td>$1.29 \times 10^{-4}$ cm/W</td>
<td>$0.028 \times 10^{-4}$ cm/W</td>
<td>$0.351 \times 10^{-4}$ cm/W</td>
</tr>
<tr>
<td>Re($\chi^3$)</td>
<td>$1.76 \times 10^6$ esu</td>
<td>$15.003 \times 10^6$ esu</td>
<td>$6.317 \times 10^6$ esu</td>
</tr>
<tr>
<td>Im($\chi^3$)</td>
<td>$0.18 \times 10^6$ esu</td>
<td>$0.1781 \times 10^6$ esu</td>
<td>$2.181 \times 10^6$ esu</td>
</tr>
<tr>
<td>$\chi^3$ susceptibility</td>
<td>$1.78 \times 10^6$ esu</td>
<td>$15.004 \times 10^6$ esu</td>
<td>$6.683 \times 10^6$ esu</td>
</tr>
</tbody>
</table>

X. CONCLUSION

The single crystals of KAP, SAP and AAP have been grown by solution technique. The single crystal XRD analysis affirmed that KAP, SAP and AAP crystals were belongs to orthorhombic system. The functional groups are dependable by FTIR analysis and the crystals KAP, SAP and AAP have good transparency. The phthalate based crystal has good thermal and mechanical stability were performed by TG/DTA and Vicker’s hardness measurement. The SHG efficiency of KAP and SAP was measured as 0.4 and 1.1 time that of KDP and the $\chi(3)$ susceptibility of KAP, SAP and AAP is 1.78, 15.004 and 6.683 x 10-6 esu.

REFERENCE


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