Growth and Characterization of Pure and Amino Acid doped KHP Crystals

T. Karpagam*a, K. Balasubramanian*

*a Research Scholar, Department of Physics, The M.D.T. Hindu College, Tirunelveli
*Department of Physics, The M.D.T. Hindu College, Pettai, Tirunelveli.
E-mail: tkarpagam1979@gmail.com

Abstract: Semi Organic Potassium Hydrogen Phthalate single crystal with amino acid L-Phenylalanine as a dopant was grown by slow evaporation technique. The grown crystals were subjected to powder XRD analysis, and the results confirm its structure and lattice parameters. The Fourier Transform confirms the incorporation of L-Phenylalanine in to KHP crystal. The optical transparency of the grown crystal was studied by UV-Visible spectroscopy. Mechanical strength of the grown crystal was estimated by Vickers hardness Test. Both dielectric constant and dielectric loss decreases with the increase in temperature at constant frequency.

Key words: Semi - organic material; X-ray diffraction; Infrared spectroscopy; optical transmittance studies; Dielectric studies;

1. Introduction

Potassium Hydrogen Phthalate, often called simply KHP (also known as potassium acid phthalate) is an interesting analyzer material in X ray spectroscopy. Recently amino acid family crystals are playing an important role in the field of non-linear optics and several new complexes incorporating the amino acid have been crystallized. In the present work, the structural, optical and thermal properties of amino acid L-Phenylalanine doped KHP crystal, which was grown by slow evaporation technique at room temperature.

2. Experimental method

The amino acid L-Phenylalanine doped KHP crystals were grown by the slow evaporation solution growth method. The KHP salt was dissolved in de ionized water. The solution was stirred well for an hour constantly using magnetic stirrer. With this solution, 0.05 and 0.13 mol % of L-Phenylalanine was added as a dopant. After homogeneous mixing solutions, it was kept in dust free area for slow evaporation.

3. Result and Discussion

After a period of time a good quality transparent single crystals of undoped and L-Phenylalanine KHP crystals were grown. Photographs of grown doped and undoped crystal are shown in fig (1).

![Fig (1). As grown crystals of KHP crystals (a). Undoped (b). 0.05mol% doped L-Phenylalanine (c). 0.13 mol% doped L-Phenylalanine](image)

3.1 Powder XRD Analysis

The grown crystals were subjected to powder XRD analysis using X’pert pro with Cu Kα1 radiation (λ = 1.54060 Å) for the phase analysis. Powder XRD patterns of the grown crystals shown in fig (2). The results confirmed that all the crystals formed in orthorhombic structure with space group Pca21 according to JCPDS data (311855). The XRD pattern shows slight changes in peak intensities and peak positions for the crystals grown in the presence of amino acid source when compared to the undoped KHP. The cell parameters of undoped and doped KHP crystals were calculated and the data are given table (1).
Fig (2). XRD pattern for KHP crystals (a) Undoped (b) 0.05 (c) 0.13 mol% doped L-Phenylalanine

Table 1: lattice parameters of undoped and doped KHP crystals

<table>
<thead>
<tr>
<th>Lattice parameters</th>
<th>JCPDS</th>
<th>Observed KHP</th>
<th>Observed 0.05M% L-Phenylalanine doped KHP</th>
<th>Observed 0.13M% L-Phenylalanine doped KHP</th>
</tr>
</thead>
<tbody>
<tr>
<td>a(Å)</td>
<td>9.605</td>
<td>9.625</td>
<td>9.6225</td>
<td>9.6025</td>
</tr>
<tr>
<td>b(Å)</td>
<td>13.331</td>
<td>13.3195</td>
<td>13.3037</td>
<td>13.2984</td>
</tr>
<tr>
<td>c(Å)</td>
<td>6.472</td>
<td>6.4603</td>
<td>6.4413</td>
<td>6.4378</td>
</tr>
<tr>
<td>volume(Å³)</td>
<td>828.8305</td>
<td>828.2139</td>
<td>824.8381</td>
<td>822.6946</td>
</tr>
</tbody>
</table>

3.2 FTIR analysis

FTIR spectrum of undoped and L-Phenylalanine doped KHP crystals were recorded using Perkin Elmer spectrum in the range 400-4000 cm⁻¹ by KBr pellet technique. The FTIR spectra of the grown crystals are given in fig(3). The FTIR spectra of 0.05 and 0.13 mol% doped crystals show strong NH symmetric stretching at 2400-2650 cm⁻¹. Where KHP is doped with L-Phenylalanine more NH stretch vibrations are introduced due to doping and the NH absorption peak become stronger. So, FTIR spectra also established the presence of L-Phenylalanine in the lattice of KHP crystals.

Fig (3). FTIR analysis for Undoped and 0.05 and 0.13 mol% L-Phenylalanine doped KHP crystals

In the FTIR spectrum, OH stretching hydrogen bond appears at 2784 cm⁻¹ for the pure and 2794 cm⁻¹, 2791cm⁻¹ for the doped compound. This shift is due to the incorporation of phenylalanine into the KHP material. This shift may also be due to the free stretching of NH₂ group present in the dopant. In addition to that, C=C ring stretching appears at 1489 cm⁻¹ for undoped and 1483 cm⁻¹, 1482 cm⁻¹ for the dopant. From the FTIR spectrum, the presence of the functional groups has been confirmed.

3.3 UV-Visible –NIR –Spectroscopy

The UV-visible –NIR spectroscopy was performed on the samples by using UV-700 SHIMADZU spectrophotometer. The recorded transmittance spectra of undoped and doped crystals in the wavelength range 200-1100 nm.
Fig (4). UV Transmittance spectra of Undoped and doped KHP crystals

Large absorptions are found at around 300 nm for undoped and doped KHP crystals due to n-π transition of the carbonyl group of the carboxyl functions. As the doping level increased the transmittance curves decrease, because interstitially occupied dopant produce dislocations in the crystals developing more gain boundaries. The recorded spectra are shown in fig (4). The value of band gap was found to be 6.7eV for KHP crystals.

3.4. Micro hardness Test

To estimate mechanical hardness, the indentation hardness is measured as the ratio of applied load to the surface area of the indentation. A plot drawn on hardness value and corresponding load is shown in Fig(5).

The harness number was calculated using the relation, \( Hv = \frac{1.8544P}{d^2} \text{Kg/mm}^2 \). Where, \( Hv \) is the Vickers hardness number, \( P \) is the applied load and \( d \) is the diagonal length of the indentation impression. It is observed that the hardness number increases with increase in load and it reveals that the doped KHP crystal exhibits reverse indentation effect. By plotting \( \log p \) versus \( \log d \), the value of the work hardening coefficient is found to be greater than 2 for pure and doped crystals. Onitsch states that the values 1.0<\( n \)<1.6 for hard materials and \( n \)>1.6 for soft materials. Hence, it is concluded that pure and doped crystals are also soft materials.

3.5 Dielectric studies

The dielectric properties are associated with the electro-optic property of materials, particularly when they are non-conducting materials. Figure (6) show the variations of dielectric constant and dielectric loss of the pure and doped crystals at different temperatures at constant frequency. The dielectric constant was calculated by using the relation \( \varepsilon_r = \frac{Ct}{\varepsilon_0A} \). Where \( \varepsilon_0 \) is the permittivity of the free space, \( C \) is the capacitance, \( t \) is the thickness of the sample and \( A \) is the area of the cross section. The decrease in dielectric constant of the pure and doped crystal at low frequencies may be attributed to the contribution of electronic, ionic, orientation and space charge polarizations which depend on the frequencies. It is further observed that both dielectric constant and dielectric loss decrease with increase in temperature.
Fig.(6) variation of dielectric constant and dielectric loss with constant frequency at different temperatures

4. Conclusion

The undoped and L-Phenylalanine doped KHP crystals were grown by slow evaporation method. XRD studies for the grown crystals have been carried out and it is found that the structures of the grown crystals are orthorhombic. The unit cell parameters of the grown crystals were obtained from XRD studies. The various functional groups and the modes of vibrations were identified by FTIR spectroscopy. From the UV-Visible spectral analysis of the grown KHP crystals, a strong absorption is observed at 300 nm for all grown crystals and the energy gap is 6.7 eV. Micro harness measurements imply that the pure and doped crystals come under the soft materials category. From the dielectric study, it is found that both dielectric constant and dielectric loss of the crystal decrease with increase in temperature.

References

[4]. Kumaresan, P; Moorthy babu, Anbarasan, P.M; optical materials. 2008, 30, 1361-1368