Structural, optical properties and effect of amino acid on growth of KDP crystals

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KDP is a well known non-linear optical (NLO) material with different applications. Most of the amino acids also exhibit NLO property. In the present study, pure and 5 wt% L-arginine mixed KDP crystals have been grown by slow evaporation technique. Good quality single crystal with dimension 14.0×8.0×3.0 mm³ was harvested after 15 days. The grown crystal was characterized by various characterizations. The lattice parameters and crystalline symmetry were confirmed by powder X-ray diffraction studies. The mixing of L-arginine was confirmed by FT-IR. The transmittance of KDP was found to increase in the presence of L-arginine. Vickers microhardness tests were performed to study the mechanical stability of the crystals.

Keywords: Growth from solution, Amino acid, Mixing, Single crystal, X-ray diffraction

1 Introduction

Potassium dihydrogen phosphate (KDP) crystals exhibit excellent electro-optical, non-linear properties and are commonly used in frequency conversion, applications such as second and third harmonic generation. The extensive investigation has been carried out to develop defect free bulk crystals for industrial applications for semiconductors and piezoelectric devices. The growth quality and optical properties of KDP crystals are affected by many factors such as additives and pH values. Recently, complexes of amino acid have been explored. Amino acids are interesting materials for NLO applications. The amino acids with inorganic salts are promising materials for optical second harmonic generations, as they tend to combine advantages of organic amino acids with that of inorganic salts. In view of these, a series of novel semi-organic crystals have been investigated, and especially the analog of L-arginine. L-arginine is one of the amino acids widely found in the animal sources, vegetable sources and biological substances. The earlier work by Parikh et al proved that L-arginine mixed KDP shows appreciable change in its thermal property. Complexes of amino acids with inorganic salts are considered to be novel materials for SHG properties and they are found most of the times to be as promising as KDP or better than it. L-arginine phosphate monohydrate, L-arginine dinitrate and many other forms of L-arginine have been investigated, but no attempt is made on large scale mixing of amino acid with KDP has been attempted. In the present work, we are reporting structural and optical properties of L-arginine mixed KDP crystals. The grown crystals are subjected to powder XRD, microhardness, UV-Vis and FTIR studies.

2 Experimental Details

Analar grade (AR) samples of L-arginine and KDP were used as raw material. The mixing of L-arginine (C₆H₁₄N₄O₂) into KDP (KH₂PO₄) was achieved by adding 5 wt% of L-arginine into saturated KDP solution. The calculated amount of the reactants was thoroughly dissolved in deionised water and stirred well for about four hours using a magnetic stirrer. Then the solution was slowly evaporated until the solvent was completely dried. Purity of salt was increased by successive recrystallisation process before the actual experiments. The vessel containing the solution was closed with perforated cover to allow free evaporation of the solvent. The pH value of the solution was about 5.2 and the crystals were optically transparent and free from macro defects obtained by self-nucleation of the saturated solution. Crystals of dimension up to 14.0×8.0×3.0 mm³ were obtained in
period of growth range 12-15 days. Colourless perfect crystals were obtained as shown in Fig. 1.

3 Results and Discussion

3.1 X-ray diffraction studies

The XRD pattern of the LAKDP was recorded using XPERT-PRO diffractometer system, finely crushed powder of LAKDP crystal was subjected to powder X-ray diffraction analysis. The sample scanned over the range 10 to 80° at the scan rate of 20/min. Figure 2 shows the XRD pattern of LAKDP crystals. This study reveals that the grown crystal of LAKDP crystal belongs to tetragonal system. The crystal was identified by comparing the interplanar spacing and intensities of the powder pattern with the JCPDS data of KDP crystal. The calculated lattice parameter values are found to change as seen from Table 1. Mixing changes the cell axes and hence the cell volume.

3.2 Fourier transform infrared analysis

The FT-IR spectra of the pure KDP and LAKDP were recorded in the range 400-4000 cm\(^{-1}\) using KBr pellet on BRUKKER IFS FT-IR spectrometer. Figures 3 and 4 show the FT-IR spectra of both Pure and L-arginine mixed KDP crystals. In the present investigation, focus is mainly on the effects of L-arginine mixing into crystal lattices of KDP crystal. The bending vibrations due to \([\text{H}_2\text{PO}_4]\) are observed in both the pure and mixed KDP in the region 400-600 cm\(^{-1}\). The P=O symmetric bending vibration gives a strong band at 538.54 cm\(^{-1}\) in the pure KDP and at 531.77 cm\(^{-1}\) in the mixed crystal. The absorption band at 909.14 cm\(^{-1}\) is due to P-O-H bending vibration. The P=O stretching vibration gives a strong band at 1299 cm\(^{-1}\) and 1314 cm\(^{-1}\) in the

<table>
<thead>
<tr>
<th>Crystal</th>
<th>(a(\text{Å}))</th>
<th>(b(\text{Å}))</th>
<th>(c(\text{Å}))</th>
<th>Cell volume (Å(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure KDP(JCPDS)</td>
<td>7.453</td>
<td>7.453</td>
<td>6.974</td>
<td>387.38</td>
</tr>
<tr>
<td>0.3% LAKDP (Ref.4)</td>
<td>7.453</td>
<td>7.453</td>
<td>6.975</td>
<td>387.38</td>
</tr>
<tr>
<td>0.4% LAKDP (Ref.4)</td>
<td>7.453</td>
<td>7.453</td>
<td>6.975</td>
<td>387.38</td>
</tr>
<tr>
<td>5% LAKDP</td>
<td>6.307</td>
<td>10.536</td>
<td>6.299</td>
<td>385.60</td>
</tr>
</tbody>
</table>

Fig. 1—5wt% mixed L-arginine KDP crystal

Fig. 2—XRD of LAKDP
mixed crystal. The absorption band at 679.45 cm\(^{-1}\) is due to the NH\(_2\) wagging in the mixed KDP crystal which is absent in the pure KDP crystal. This is due to the linkage of P with NH group of the amino acid, which confirms the presence of \(\text{L-arginine}\) in the mixed crystal. The C-H stretching vibration observed at 3008.22 cm\(^{-1}\) in the mixed crystal is absent in pure KDP. In mixed KDP absorption band at 1687.67 cm\(^{-1}\), is due to C=O stretching vibration. The symmetric stretching vibrations of N-H and NH\(_2\) stretching vibrations give bands in the region 3184-3374 cm\(^{-1}\) in the mixed crystal which is absent in the pure crystals which also confirms the presence of amino acid into the crystal lattice. The percentage increase in transmittance of mixed when compared with the pure KDP crystal in the entire IR spectrum is worth noting.

3.3 UV-Visible spectral study

A good optical transmittance is desirable in an NLO crystal since the absorptions, if any, in an NLO material near the fundamental or the second harmonic will lead to the loss of conversion efficiency in those wavelengths. Absorption spectra of NLO material play a major role in device fabrication\(^1\). Wider the transparency window more will be the practical applicability of that material. To find the transmission range LAKDP, the optical absorbance spectrum of the LAKDP was recorded for the wavelengths region 190-1100 nm as shown in Figs 5 and 6. From the spectrum, it is evident the LAKDP crystal has UV cut-off below 300 nm, which is sufficiently low for SHG and laser radiation at 1064 nm or other application. The mixing of amino acid does not affect the transparency of the grown crystal. The decrease in absorbance for LAKDP in comparison to pure KDP is likely due to the improvement in NLO property\(^{12}\) that LAKDP crystal has UV cut-off 235 nm which is suitable for SHG laser radiation of 1064 nm which makes it suitable for optical and NLO applications. The large transmission in the visible region enables it to be a potential candidate for optoelectronic applications\(^{13}\).

3.4 Microhardness measurement

One of the important properties of any device material is its mechanical strength, represented by its hardness. Physically, hardness is the resistance offered by a material to localized plastic deformation (movement of dislocations) caused by scratching or indentation. The indentation hardness is measured as the ratio of applied load to the surface area of the indentation. Indentation hardness measurement can, in principle, be carried out at fairly high loads.
Fig. 4—FTIR spectra LAKDP crystal

Fig. 5—Absorption spectra of pure KDP
Fig. 6—Absorption spectra of LAKDP

Fig. 7—Vicker’s microhardness of grown crystals

(1 100 kg). But for materials which have low hardness and are available as small-sized sample, it is convenient to make measurements at low loads of <200 g. The low load hardness is called microhardness. Microhardness measurement is a general microprobe technique for assessing the bond strength and the bulk strength. The crystal slices are well polished with a thickness variation less than 10 μm.

Figure 7 shows the hardness of pure KDP and LAKDP crystals. The well polished crystals were mounted on the platform of the microhardness tester and loads of different magnitudes (25-100 g) were applied over a fixed interval of time. The indentation time was fixed as 15s. In the KDP crystal, there are noticeable increase in the hardness of the crystals. By mixing of L-arginine to crystallization media, there is a gradual decrease in the crystal hardness of KDP. It was also observed that there is a significant formation of crack. On further increase of the load beyond 100 g, cracks developed on the surface of the pure KDP and LAKDP crystal due to the release of internal stress generated locally by indentation. The work hardening coefficient value (n) of the pure KDP and the LAKDP crystal was determined from the plot of log P versus log d by least square fit method. The value of n is found to be 2.65 for pure KDP and it was improved to 5.08 for LAKDP crystal.

4 Conclusions
Optically transparent, LAKDP crystal with dimension of about 14.0×8.0×3.0 mm³ was grown by slow evaporation method using water as the solvent. Powder X-ray diffraction data reveals that the LAKDP crystals belong to tetragonal system. The FT-IR analyses confirm the presence of various functional groups. The lower cut-off wavelength for LAKDP crystal (235 nm) is observed. The
UV-vis-NIR spectrum confirms its suitability for SHG applications. The second harmonic signal strength and the second harmonic generation efficiency increase as the mixing concentration of L-arginine increases. From microhardness study, it was found that the hardness of LAKDP crystal has been improved.

References