Effect of L-arginine, L-histidine and glycine on the growth of KDP single crystals and their characterization

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Optically good quality single crystals of pure and amino acid doped KDP have been grown by slow evaporation method at constant temperature (40°C). The effect of amino acid dopants on the growth and characterization of KDP crystals has been studied. The grown crystals are characterized by density, melting point determination and X-ray powder diffraction. The presence of functional groups of crystals are qualitatively analysed from FTIR spectra. Thermal properties like decomposition temperatures and weight loss have been reported from the TGA and DTA analysis. The transparency of the grown crystals has been confirmed using UV-Vis spectra. It has been found that SHG efficiency of KDP, containing amino acids is higher than pure KDP crystals. Dielectric behaviour of pure and doped samples has been studied at a temperature range 30 - 180°C and a constant frequency 1 kHz.

Keywords: Potassium dihydrogen phosphate crystals (KDP), L-arginine, L-histidine, Glycine, Non linear optical crystals (KLO)

1 Introduction
Since the discovery of second harmonic generation of ruby laser radiation in a quartz crystal by Franken1 in 1961, the search for new crystals with good frequency conversion properties continues even today. The very first material to be used and exploited for their non linear optical (NLO) and electro-optic (EO) properties was potassium dihydrogen phosphate KH2PO4 (KDP). With the aim of improving the SHG efficiency of KDP, research workers have attempted to modify KDP crystals by doping different type of impurities. There are only few reports available on the effect of amino acid on the NLO efficiency of KDP crystals. KDP doped with amino acids like α-alanine, β-alanine, α-leucine, α-histidine, α-cystine and α-valine were reported2. In this paper the growth and characterization of the L-arginine, L-histidine and glycine doped KDP crystals has been reported.

2 Materials and Methods
2.1 Crystal growth
Analytical reagent grade (AR) samples of KDP, L-arginine, L-histidine and glycine along with triple distilled water were used for the growth of single crystals. Saturated solutions of KDP doped with L-arginine, L-histidine and glycine of different mole concentrations (0.01M, 0.05M and 0.1M) have been crystallized by the low- temperature solution growth technique at 40°C in about two weeks. The grown crystals are shown in Fig.1.

2.2 Characterization
The KDP crystals modified with L-arginine, L-histidine and glycine were characterized by XRD, FTIR, thermal analysis, optical transmission spectra and dielectric measurements. The SHG intensity of the samples were tested by the modified version of the powder technique developed by Kurtz and Perry3 using Quanta Ray Spectra Physics model: Prolab 170 Nd: YAG 10 ns laser with a pulse repetition rate of 10Hz working at 1064nm.

3 Results and Discussion
3.1 Density and melting point measurements
The observed density (by floatation method, within an accuracy of ±0.01) of pure KDP (2.29gm/cc) agreed well with the reported (2.338gm/cc) value4. The density values were altered to 2.35gm/cc (L-arginine+KDP), 2.36gm/cc (L-histidine+KDP) and 2.34gm/cc (Glycine+KDP). The observed variation of density of KDP crystal caused by amino acid addition indicates that the impurity molecules have entered into the lattice of KDP crystals. The melting point was observed (TEMPO melting point apparatus) as 254°C (pure KDP), 251°C (L-arginine+KDP), 249°C (L-histidine+KDP) and 248°C (Glycine+KDP). The observed variation of density of KDP crystal caused by amino acid addition indicates that the impurity molecules have entered into the lattice of KDP crystals. The melting point was observed (TEMPO melting point apparatus) as 254°C (pure KDP), 251°C (L-arginine+KDP), 249°C (L-histidine+KDP) and 248°C (Glycine + KDP) respectively. The error in the measurement was ±1°C.

3.2 X-Ray diffraction analysis
Potassium dihydrogen orthophosphate, KH2PO4 (KDP) has a tetramolecular unit cell having
dimensions $a=b=7.448\text{Å}$ and $c=6.977\text{Å}$. Using the tetragonal crystallographic equation the lattice parameter values of pure and amino acid doped KDP crystals are calculated within an accuracy of ±0.002. The lattice parameters of doped crystals were altered as $a=b=7.424\text{Å}$ and $c=6.955\text{Å}$ (L-arginine+KDP) crystals, $a=b=7.459\text{Å}$ and $c=6.971\text{Å}$ (L-histidine+KDP) crystals and $a=b=7.460\text{Å}$ and $c=6.985\text{Å}$ (glycine+KDP) crystals. The crystals were identified by comparing the interplanar spacing and intensities of the powder pattern with the JCPDS data of KDP crystals. The variation in lattice parameters and d values for the doped samples can be attributed to the accommodation of the impurity in the crystal lattice. The slight shift in the 20 values of doped crystals suggest that crystal structure were slightly distorted compared to pure KDP crystal.

3.3 FTIR analysis

The FTIR analysis of pure and doped crystals confirms the fundamental functional groups and their vibrational modes of KDP crystals. In the spectra of amino acid doped crystals, some bands of $[\text{H}_2\text{PO}_4]$ overlap with amino acid vibrations. Hence few bands of dihydrogen phosphate ion become broader and some of the frequencies are slightly shifted. The asymmetric stretching vibrations of $\text{NH}_3^+$ of amino acid appear in the region 3100-3450 cm$^{-1}$. Some of them overlap with the OH stretching vibrations of dihydrogen phosphate ion. The symmetric deformation of $\text{NH}_3^+$ ion appears at around 1500 cm$^{-1}$ in the spectra of all doped crystals with medium intensity. The CH$_3$ bending vibrations of amino acids appear around 1450 cm$^{-1}$. These vibrations of amino acids present in the spectra of doped crystals reveals the incorporation of impurities in the crystals.

3.4 Thermal analysis

The TGA curves of pure and doped KDP samples are shown in Fig. 2. These studies reveal that pure KDP is thermally stable up to 310°C, after which the sample undergoes an appreciable weight loss. The weight loss is about 12.85% and this corresponds to the loss of one water molecule. But in the case of L-arginine, L-histidine and glycine doped KDP crystals, decomposition temperatures were shifted to 328, 319 and 323°C. The marginal increase in temperature is evident for doped crystals, suggesting that the substitution of amino acids enhances the thermal stability of KDP crystals. The DTA curves of pure and amino acid doped KDP crystals are shown in Fig. 3. In the case of pure KDP crystals it is found that there is an endothermic peak at 193.69 °C, which may correspond to the so called high temperature phase.
transition. On heating further, some other endothermic peaks are formed at 245.09 and 271.84ºC. In L-arginine doped crystals the small endothermic peak at 193.69ºC corresponding to the phase transition temperature of pure KDP crystal is missing, whereas other endothermic peaks were shifted to 238.68 and 268.2ºC respectively. For L-histidine doped KDP crystals, endothermic peaks were shifted to 198.01, 242.21, and 278.61ºC. But in the case of glycine doped crystals endothermic peaks are obtained at 196, 235.81 and 270.72ºC. It is concluded that the amino acid provides a favourable root to produce crystals with better thermal stability.

3.5 Powder SHG measurement

The SHG studies were carried out in pure KDP and doped samples. The signal amplitude in milli volts indicates the SHG efficiency of the sample. Anandakumari and Chandramani have shown that the second harmonic generation efficiency is found to be appreciably increased by the addition of alkali halides as impurities. Authors have observed second harmonic signals of 164mV (pure KDP), 198mV (L-arginine+KDP), 175mV (L-histidine+KDP) and 180mV in (glycine+KDP). This study has revealed that \( I_{2\omega} \text{(KDP)} < I_{2\omega} \text{(KDP+ L-histidine)} < I_{2\omega} \text{(KDP + glycine)} < I_{2\omega} \text{(KDP+ L-arginine)} \). It shows that doping of amino acids in definite ratios enhances the NLO efficiency of the KDP crystals. Due to substantial number of defects formed due to the doping, one can expect an enhancement of SHG signals.

3.6 Optical transmission studies

For optical applications, especially for SHG, the material considered must be transparent in the wavelength region of interest. Optical transmission spectra recorded for the samples of pure as well as 0.1M amino acid doped crystals are shown in Fig. 4. The UV-visible spectra reveal that transmittance is nearly 99% between 200 and 1000nm. As the entire region does not bear any absorption band, it shows good transparency in the visible region so that it can be used for NLO applications. The amount of transmittance has increased via pure KDP, KDP with L-arginine, KDP with L-histidine and KDP with glycine respectively. It is also seen that the cut off
wavelength is almost same for pure and doped crystals.

3.7 Dielectric measurements

Dielectric measurements were carried out in the temperature range 30 - 180°C at constant frequency of 1kHz. Knowing the capacitance and diameter of the pellet, the dielectric constant was determined and is shown in Fig.5. It shows that dielectric constant is found to increase with temperature. Dielectric values of doped crystals were less than those of pure KDP crystals. The lower value of dielectric constant is a suitable parameter for the enhancement of SHG signals.

4 Conclusions

Transparent, colourless crystals of pure and L-arginine, L-histidine and glycine doped KDP single crystals were grown by slow evaporation technique at 40°C. Powder X-ray diffraction studies, evaluation of lattice parameters and density measurements, confirm that the dopants have gone into the lattice of the crystals. This study reveals that slight distortion in the unit cell with a decrease in volume in all doped crystals. The FTIR study confirms the presence of amino acids in the doped crystals. TGA and DTA analyses reveal the different stages of decomposition. Thermal stability of the doped crystals is found to increase due to doping of amino acids. The transmission spectra reveal that amino acid additives have not destroyed the optical transparency of the crystals and have sufficient transmission in the entire UV-visible and IR regions. Amino acid doped crystals have shown an increase in SHG efficiency compared to pure KDP crystals. It has been observed that addition of amino acid enhances transparency, thermal stability and NLO efficiency of KDP crystals. The dielectric study reveals that amino acid addition reduces the values of KDP crystals.

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