DIFFRACTION, FT-IR STUDIES OF AMINO ACID DOPED POTASSIUM DIHYDROGEN PHOSPHATE (KDP) SINGLE CRYSTAL BY MODIFIED CTB THERMOMETER

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Abstract

Due to very large polarizability and wide transparency window, semiorganic NLO materials have alternative to inorganic materials because of their efficient molecular nonlinearity over a broad frequency range, low cost, low refractive index, low dielectric constant, inherent synthetic flexibility, moderate optical damage density, fast response with the better process ability and ease of fabrication into devices. A Semi organic crystal of amino acid (valine) doped KDP (KH2PO4) have grown by modified CTB thermometer as well as by rotating seed crystal method (RSCM). The concentration of dopants was altered in every step for different rotation rate. The good quality transparent crystals has been harvested; the dimensions of grown crystal observed from 1mm to 4 cm. crystalline perfection, all lattice parameter of grown single crystal have been determined by powder X-ray diffraction analysis. The functional groups of LV doped KDP were identified using vibration spectra analysis. The chemical composition as weight percentage (wt %) of C, N, K, P and O as obtained from EDAX analysis. A quantitative interpretation of influence of amino acid L-valine verified by mathematical model usually describes a system by a set of variables and a set of equations that establish relationships between the variables.

Key Words : crystal growth, XRD, FT-IR, EDAX analysis.

1. Introduction

Non-Linear Optics in which the dielectric polarization P responds nonlinearly to the electric field E of the light. This nonlinearity is typically only observed at very high light intensities such as those provided by lasers. KDP is a representative of hydrogen bonded materials which posses important piezoelectric, ferroelectric, electrooptic and mainly NLO properties. [1]. Due to their potential application NLO materials was of widely used in optical devices.

In present communication, the doped crystal of KDP by valine amino acid had been prepared by modified CTB as well as by SRCM. Initially pure KDP seeds crystal was prepared by slow cooling and slow evaporation of saturated solution in a clean controlled temperature enclosure. The amount of KDP in a solvent (water) can be calculated by using solubility curve of Pure KDP and the amount of solute (m) for different concentration of dopant can be calculated by using mole percentage formula.

The SR method setup has been modified in some aspects in order to grow clear bulk size KDP crystals. A glass ampoule was designed and fabricated at laboratory for the growth of KDP single crystal, by modifying the CTB using spiral glass tube of heating in SR method shown in figure 1. Especially design Spiral glass tube used to surround the bottom of glass ampoule to maintain constant temperature during growth of crystal. A clean defect frees Seed along (100) plane which was fixed by mounted at the bottom of the ampoule in such a way that the seed should be tight at the end of ampoule to avoid bidirectional growth of crystal from the surround area of crystal. The face was exposed to the solution of LVKDP so that the growth of bulk size crystal can be initiated. The solvent get was saturated using pH- 4.8 for L-valine [2-5]. The top open face of the ampoule was covered by a thick plastic sheet with a hole at the center for facilitating controlled evaporation of the solvent. The whole setup was placed in a zero vibration zone area. After 15 days a good quality transparent crystal of LVKDP was observed with growth rate 2mm per day for 10-12 days and dimension reached up to 40 mm in height is shown in figure 2.

Fig. 1 : CTB tank with spiral glass tube of heating in SR method
2. Material and Method

2.1 Crystal Growth

Merck A.R grade sample of KDP along with triple filter deionized water (Millipore 18.2 MΩ/cm resistivity) were prepared for the growth of crystals. Solution was prepared according to solubility curve of KDP at the constant growth temperature in under saturation condition, which was thoroughly stirred for 5 to 6 hours for homogenization at using a temperature controlled magnetic stirrer with hot plat to get homogeneous mixture of solution. The Solution is now homogeneous and attained near supersaturation level at room temperature. Then solution is filtered with Whatman filter paper of pore size 11 μm and kept in the 500 ml beaker cover with polythene by making 10 to 15 holes. Solution is allowed to evaporate at the room temperature in a dust free environment. After a period of few weeks, colorless and transparent seed crystals were harvested. Approximately after 20-30 days tiny seed crystals were observed in beaker. The size of seed crystal grown was observed in the size of 4mm up to 18 mm. these seeds used are used to grow bulk size crystal by two methods. Viz. SRCM and SR (Shankarnarayan Ramasamy)-Method. [6-8].

2.2 Seed Rotating Crystal Method

Firstly processed seed is placed on cylindrical platform which was made by using acrylic sheet The cylindrical platform attached with rotating unidirectional DC motor ,which were controlled by electronic dc power supply of 12 V about 20 rpm and 60 rpm. Whole assembly placed on rectangular constant temperature bath which was made by glass plate. Constant temperature controller were used which was maintained at 400C and 450C

The KDP growth rate is approximately 1mm per day is observed. A good transparent quality of crystal is obtained. High rotation might damages the heavy crystal, which easily causes spontaneous nucleation and therefore terminate the growth [9]. The solubility of pure KDP in demonized water was assessed as a function of temperature in the range 30–500 C.

3. Result and Discussion

3.1 XRD analysis

Single crystal X-ray diffraction analysis for the grown crystals has been carried out to identify the cell parameters using an ENRAF NONIUS CAD 4 automatic X-ray diffractometer. Calculated lattice parameters are listed in table 1. These values are found to agree with the reported values [10].

| Chemical formula | KH₂PO₄ |
|------------------|--------|
| Molecular weight | 136.086 gm/mole. |
| Crystal system   | Tetragonal |
| Space group      | I42d |
| Space Group no   | 122 |
| a=b (Å)          | 7.4532 Å² |
| c (Å)            | 6.9742 Å² |
| α=β=γ            | 90° |
| Cell volume      | 387.42 |
| Z                | 4 |
| JCPDF no         | 035-0807 |
| Melting point    | 252.6°C |

Fig. 2 : Grown crystals of different concentration

Fig. 3 : X-ray density

Fig. 4 : Porosity of grown crystal
The evaluation of lattice parameters and density measurements, it is confirm that the dopants have gone into the lattice of the crystals. This study reveals that slight distortions in the size of unit cell with a decrease in volume in all doped crystals were observed. The porosity of doped KDP crystal decreases as the concentration of L-valine dopant in pure KDP increase. This reveals the Charge may get transfer from amino acid to KDP [11]. As concentration increases lattice parameters decreases which leads to decrease porosity also observed. Shown in figure 3.4.

3.2 FTIR Spectral Analysis:

The frequencies with relative intensities obtained from FTIR specral analysis. The frequencies have been observed at 3437 cm\(^{-1}\) represent OH streching ,which represent NH3 group present in compound. 1644 cm\(^{-1}\) shows P=O-H streching, 538.16 cm\(^{-1}\) represent HO-P-OH and 902.94 cm\(^{-1}\) represent O=P-OH stretching, 1297.51 cm\(^{-1}\) represent C-H bonding , 1644 cm\(^{-1}\) shows O=OH streching, which represent OH3 group present in compound. Wave number 1297.51 cm\(^{-1}\) represent C-H bonding . IR spectra indicates that the valine dopant affect on the KDP. The broad absorption band appeared at 3372, 3454 were assigned to hydrogen bonded O–H stretching frequencies in 2.0 and 0.8 mole % doped KDP. This peaks absent in 1.0 mole %. This lead to the decrease in the frequency of O–H stretching and confirmed the non-linear optical property of pure and doped. This property is also reflected in the P=O, P–O, P– OH streching and HO–P–OH bending vibrations shown in Table 2. The vibration assignments showed the hydrogen bonding results in stretching frequencies of O-H group of KDP and the carboxyl group of L-valine molecules. This confirms the presence of L-valine into pure KDP crystal [12-15].

3.3 Thermal Study

Thermal stability is very important parameter of single crystal. Hence TGA /DTA studies are used to investigate the melting behavior, Glass Transition, Crystallization, Oxidation Stability, Kinetics, Purity, and Specific Heat of grown sample of pure and doped KDP. Thermal analyzer is analyzed at the heating rate 10 0C/ min ranging from 30 to 300 0C in the inert nitrogen atmosphere.

![Fig. 5 : TGA curve of doped KDP crystal](image)

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| Sr. No | Calculated frequencies (cm\(^{-1}\)) | Pure KDP (cm\(^{-1}\)) | 0.8% LV +KDP (cm\(^{-1}\)) | 1.0% LV +KDP (cm\(^{-1}\)) | 2.0% LV +KDP (cm\(^{-1}\)) | Assignments |
|-------|-----------------------------------|-----------------------|-----------------------------|-----------------------------|-----------------------------|-------------|
| 1     | -                                 | 3605                  | --                          | --                          | 3572.41                     | Free O–H stretching Hydrogen bonded of KDP |
| 2     | --                                | 3333                  | 3472.45                     | --                          | 3454.46                     | O–H stretching Hydrogen bonded of KDP |
| 4     | 2839                             | 2844.65               | 2824.74                     | 2820.7                      | 2806.75                     | P–O–H symmetric stretching |
| 5     | 2461                             | 2484.24               | 2468.40                     | 2460                        | 2460                        | NH\(_3\) bending superimpose d with P–O–H stretching |
| 6     | 2358                             | 2362.94               | 2362                        | 2366.89                     | 2366.89                     | P–O–H bending of KDP |
| 7     | 1718.49                          | --                    | --                          | --                          | C–O stretching |
| 1650  | 1671.25                          | 1693.2                | 1635.27                     | O–P–OH stretching of KDP |
| 8     | 1295                             | 1297.39               | 1299.42                     | 1295.42                     | P–O–H stretching of KDP |
| 9     | 1100                             | 1095.92               | 1097.51                     | 1095.51                     | P–O–H stretching of KDP |

The TGA curve (figure 5) sharply decrease at temperature at 2200 C it means crystal is thermally stable up to 2200 C and thereafter crystal decomposes at 3500 C. The weight loss curve is very sharp and it starts at 2200 C and ends at 3500C. This weight loss is due to the liberation of volatile substances. The curve sharply decreases at temperature at 2200 C and 3500 C is most probable melting point of KDP crystal. This shows that the presence of l-valine appears to increase the decomposition temperature of KDP. The DTA curve (figure 6) shows an endothermic peak at 220.20 0C, 263.85 0C, 323.5 0C. But the intensity of satellite peak is very less this result indicates the dopant
L-valine is incorporated in the crystal lattice which improve the stability in the presence of L-valine (P. Kumaresan 2008). Enthalpy $\Delta H$ changes in the endothermic reaction are 241.44 J/gm, 63.75 J/gm. 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 they melt with decomposition at high temperature [16-24].

3.4 Vickers's Microhardness Analysis

Hardness is a measure of a material's resistance to localized plastic deformation. The mechanical property of the material is useful for determination for device fabrication and it is directly related to its bonding and crystallographic orientation. Vickers indentation test studied by Mitutoyo Microhardness tester on cut and polished plate of (100) plane of thickness 5 mm in size with load using Vickers hardness tester with diamond indenter attached to an incident light microscope and the indentation time was kept as 20 sec for all loads. Crystals with flat and smooth faces, microscopically free from signs of any damage are selected for indentation studies. The indented impressions are approximately pyramidal in shape. The distance between two indentation points was maintained to be more than three times the diagonal length, in order to avoid any mutual influence of indentations. N. Karthick et al reported the formula for calculation of Vicker's microhardness number $H_v$.

Table 3 shows the Vickers hardness ($H_v$) for the 1.0 mole% and 2.0 mole% of L-valine doped KDP crystals at constant load. At 50 g the $H_v$ of doped KDP was found 120.4 Hv and 122.0 Hv. This shows that the concentration of dopant increases the hardness property of crystals. Table 4 shows the Vickers hardness ($H_v$) of doped KDP crystal for varying applied load as 10gm, 25gm, 50gm & 100gm.

From the study, it was observed that there is an increase in the hardness with load, which can be attributed to the work hardening of the surface layer. Beyond a load of 100 gm, significant cracking occurs, which may be due to the release of internal stresses generated locally by indentation and hence hardness value.

4. Conclusion

The calculated unit cell parameters of grown crystals are $a = b = 7.428\,\text{Å}$, $c = 6.934\,\text{Å}$, are in good agreement with the result reported in literature. The study of XRD reveals the crystal structure of KDP remains same by doping valine acid. The concentration of dopant increases the X-ray density. There are high similarities between the spectra of pure and L-valine doped KDP. Also, for low concentration of dopant pure KDP peaks are predominant over valine peaks. TGA curve sharply decrease at temperature at 230ºC it means crystal is thermally stable up to 230ºC and after this crystal decomposes at 356ºC and completely decomposes at 726ºC. DTA graphs show the peaks at 219.70ºC, 265.39ºC, 297.01ºC and 323.95ºC which reveal endothermic reaction. Enthalpy $\Delta H$ changes in the endothermic reaction are 241.44 J/gm, 63.75 J/gm. The Vickers hardness value increases as dopant concentration increases due to stiffness of grown crystal which has low porosity.

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