



Chemical Etching Studies of Pure and Amino acids Doped KDP Crystals

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Abstract: Potassium dihydrogen phosphate (KDP) and amino acids are non-linear optical material used for laser frequency conversion. The pure and amino acids (L-arginine, L-lysine and L-alanine) doped KDP crystals were grown by slow solvent evaporation technique. The amino acid doping was confirmed by CHN analysis, paper chromatography and FTIR studies. The (100) face of pure and amino acids doped KDP crystals were selected for the chemical etching studies. The etchant used for all crystals were glacial acetic acid (CH_3COOH). The etching temperature was varied from 25 °C to 40 °C with increment of 5 °C. The etch pits was measured and Arrhenius law applied. The values of kinetic and thermodynamic parameters were evaluated from width of etch pit.

Keywords: Dislocation, Etch pits, Reactivity, Kinetic parameter and Thermodynamic parameter.

1 Introduction:

Reactivity of solids is of practical and fundamental importance. In some cases, for example, propellants, heterogeneous catalysis, etc., high reactivity is required; whereas, the low reactivity is a need in oxidation and corrosion of materials. The study of reactivity of crystals is mainly carried out by preferential etching and gross dissolution. The preferential etching is subjected to the qualitative analysis of the defects sites of a crystalline solid and, thereby, indicates the quality or perfection of the crystal. Etching though a simple and widely adopted technique for the study of imperfections in a large variety of crystalline materials, the process is still not very well understood.

There are numerous researchers who have carried out chemical etching studies on KDP crystals with different aims. Usually, the water-soluble crystals find water as a good etchant. Water easily produces etch pits on these crystals. The etching capability decreases along the series of homologous alcohols and acids with addition of a $-\text{CH}_2$ group. The change in the solvent not only changes the etching capability but also the etch pit morphology and also the different surfaces behave differently to the same series of solvents. This has been discussed elaborately by Sangwal [1]. Balamurugan et al have reported etching study of KDP crystals on (100) faces with water as an etchant at room temperature [2]. They observed elongated rectangular etch pits with dislocation density of the order of 10^2 cm^{-2} . Ravi et al have reported rectangular etch pits on (100) planes of deuterated KDP crystals by unsaturated solution as an etchant and obtained the dislocation density of about $5 \times 10^3 \text{ cm}^{-2}$ [3].

Chemical etching technique has also been used to reveal certain surface features, for instance, hillocks and etch spirals. When dissolution of the crystalline surface takes place on wide spread and leaving a few

undissolved specific parts, it forms hillocks having just opposite nature to the etch pits. Gupta et al chemically etched prismatic (100) faces of gel grown KDP crystals and observed the presence of hillocks and etch spirals [4]. Both screw and edge dislocations were clearly identified by selecting suitable etchants. Javidi et al used water as an etchant and selected 3 second etching time for etching slice of (101) face of KDP [5]. They observed concentrated triangular etch pits. Another etchant they selected was acetic acid saturated with KI salt and etched for 90 second, which produced rectangular shaped etch pits. However, the orientation of the etch pits on (100) face was different for each etch pits. The etching experiments showed that the appearance of etch pits on the (100) and (101) faces by different etchants with the same morphology took place. They concluded that the etch pits were due to surface dislocations.

The effect of environment has also been studied on the crystalline face of KDP crystals. Wheeler et al have investigated the etch pits formation on KDP crystals with sol-gel based anti reflection coatings [6]. They found that the etch pits were produced beneath the sol-gel coating after the exposure to ambient humidity. The etch pits were uniformly distributed and their sizes were found to be governed by relative humidity and the thickness of the coating. Water absorbed from the environment in to the porous sol-gel coating came to the contact of crystalline surface, causing the etch pit nucleation at high under saturation with their facets correspond to the low energy planes of KDP crystal. It would have been an incomplete introduction, if the present authors had not mentioned the efforts made by Sangwal and his colleagues to understand chemical etching of crystalline faces, particularly on KDP crystals [7-9].

In the present study pure and amino acids (L-arginine, L-lysine and L-alanine) doped KDP crystals were subjected to chemical etching on their (100) as grown faces. The kinetic and thermodynamic parameters are evaluated for the motion of ledges of the etch pits to understand the effect of doping on reactivity at line defects.

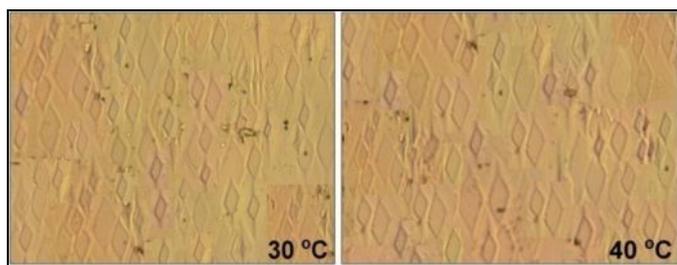
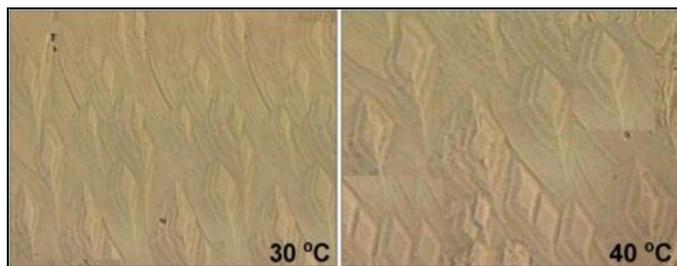
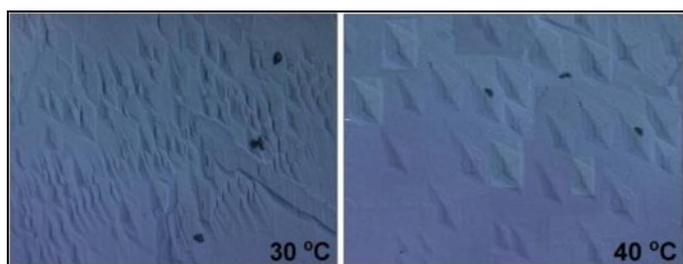
2 Experimental:

The pure and amino acids (like as; L-arginine, L-lysine and L-alanine) doped KDP crystals were grown by slow solvent evaporation technique, which has been discuss in details for L-arginine [10], L-Lysine [11], L-alanine [12] doped KDP crystals earlier by us. The presence of respective amino acid in KDP crystals was determined by CHN analysis, FTIR spectroscopy and paper chromatography using ninhydrin, which was already reported earlier for each doping system. The (100) face of pure and amino acids doped KDP crystals selected for the chemical etching studies. The etchant used for all crystals were AR grade glacial acetic acid (CH_3COOH). For every etching process, fresh etchant was used. The etching time was selected 10 second. For high temperature etching, the beaker containing etchant was heated by using suitable water bath of ± 0.1 °C accuracy and the crystal was dipped into the etchant for 10 second and thereafter, removed and air dried before observation under microscope. A soft tissue cleaning was also done before air drying. The etching temperature was varied from 25 °C to 40 °C with increment of 5 °C. Standard tests have been conducted to identify that the selected etchant reveals dislocation etch pits [13]. The etch pits were observed by using Carl Zeiss NU2 microscope. For the measurements of etch pits width a filar eye-piece attached with microscope was used with 0.005mm micrometer. The photomicrographs were recorded using AxioCam 506 mono CCD camera with 2.0 mega pixels.

3. Results and discussion:

3.1 Etch-pits observation:

Photomicrographs of etch pits observed on (100) faces of pure and 0.3 wt % L-arginine, L-lysine and L-alanine doped KDP crystals etched at 30 °C and 40°C are shown in figures (1) to (4) respectively. From the figures (1) to (4) of pure and selected amino acids doped KDP crystals, one can see that the etch pits are rhombic in nature. Some of the etch pits are flat bottom and with blunt edges, which are likely to be due to doped impurities and thus may decorate the presence of doped compounds.

Fig. 1 Etch pits of pure KDP crystal on (100) face at 30 °C and 40 °C.**Fig. 2** Etch pits of 0.3 wt. % L-arginine doped KDP crystal on (100) face at 30 °C and 40 °C.**Fig. 3** Etch pits of 0.3 wt. % L-lysine doped KDP crystal on (100) face at 30 °C and 40 °C.**Fig. 4** Etch pits of 0.3 wt. % L-alanine doped KDP crystal on (100) face at 30 °C and 40 °C.

3.2 Kinetic Parameters:

During the etching study of alkali halide crystals by various solutions, it has been found that nature of solvent, nature and concentration of impurities, temperature, stirring, under saturation, crystallographic orientation of the surface being etched, segregation of impurities at dislocations and type of dislocations affect the formation of etch pits [8]. Moreover, Sangwal has reported the roles of crystal structure, solvent surface orientation, additive impurities and reaction products in etching [7].

The Arrhenius equation is usually used today to interpret kinetic data, in chemical etching, i.e. the temperature dependence of etch pit width

$$W = Ae^{-E/RT} \quad \text{or} \quad \log W = \log A - E/RT \quad (1)$$

Where, W = Average width of etch pit, A = Pre-exponential factor, E = Activation energy of the reaction, R = Gas constant, T = Absolute temperature

The Pre-exponential factor or frequency factor is related to the collision frequency and the steric factor. Boikess and Edelson [14] describe that the value of A increases if the steric factor increases or collision frequency increases. In other words, a reaction will be faster if there are more collisions or a higher percentage of the collisions which have the proper orientation required for product formation. The specific rate constant or the average etch pit width (W) is high for fast reactions. It is evident from the above expression that as E , the activation energy, increases, the value of W decreases and consequently the reaction rate decreases. The

activation energy is considered as a barrier to be surmounted to form the reaction product. Therefore, higher the values of activation energy slower are the reaction rate.

In the present investigation, flat bottom rhombus etch pits, in all cases including pure KDP were obtained. More than 25 etch pits were measured to find the average etch pit width (W). The Arrhenius plots of $\log W$ versus $1/T$ for pure and L-arginine, L-lysine and L-alanine doped KDP crystals are shown in figure (5) to (7) respectively. The values of activation energy and pre-exponential factors were calculated using equation (1) for pure and amino acids doped KDP crystals. Table (1) summarizes the values of activation energy and pre-exponential factors calculated for pure and amino acids doped KDP crystals.

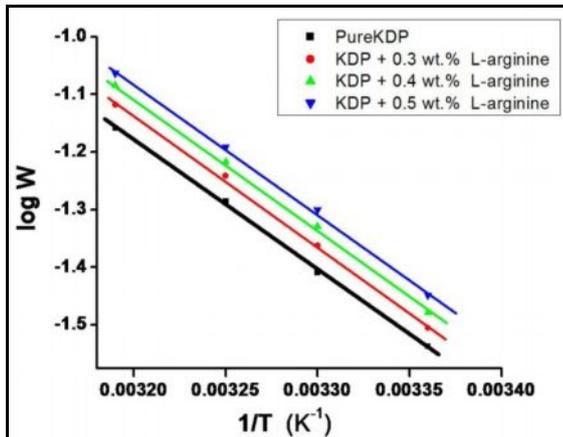


Fig. 5 Plot of $\log W \rightarrow 1/T$ for pure and L-arginine doped KDP crystal.

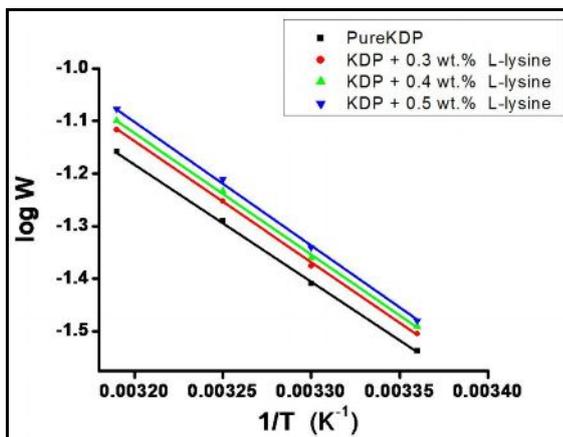


Fig. 6 Plot of $\log W \rightarrow 1/T$ for pure and L-lysine doped KDP crystal.

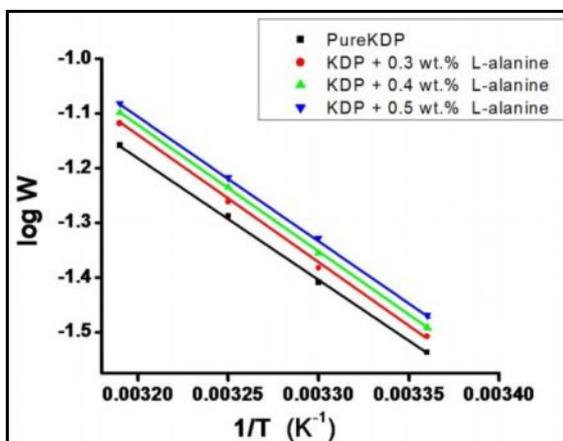


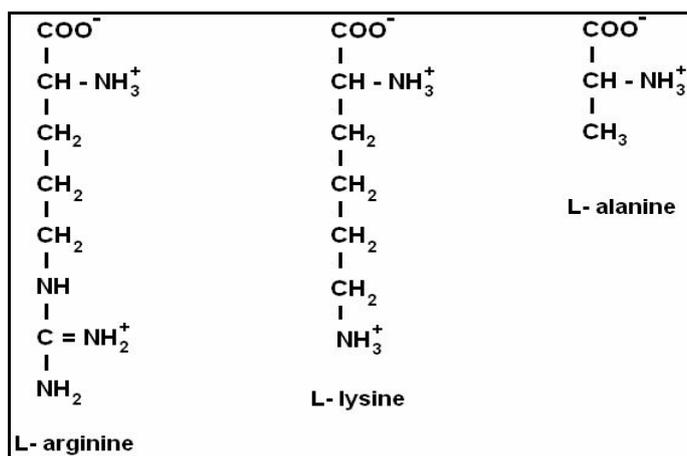
Fig. 7 Plot of $\log W \rightarrow 1/T$ for pure and L-alanine doped KDP crystal.

Table 1 Kinetic and Thermodynamics parameters for pure and amino acids doped KDP crystals.

| Sample | Activation Energy kJ mol ⁻¹ | Pre-Exponential Factor | Standard Entropy JK ⁻¹ mol ⁻¹ | Standard Enthalpy kJ mol ⁻¹ | Standard Gibbs free Energy kJ mol ⁻¹ | Change of Standard Internal Energy kJ mol ⁻¹ |
|---------------------------|-------------------------------------------|------------------------|--------------------------------------------------------|-------------------------------------------|----------------------------------------------------|------------------------------------------------------------|
| Pure KDP Crystal | 21.95 | 1.96 x 10 ⁷ | -45.93 | 16.92 | 30.83 | 22.33 |
| KDP + 0.3% wt. L-arginine | 20.11 | 4.34 x 10 ⁶ | -53.17 | 15.08 | 31.19 | 20.55 |
| KDP + 0.4% wt. L-arginine | 20.05 | 5.39 x 10 ⁶ | -52.15 | 14.92 | 30.72 | 20.38 |
| KDP + 0.5% wt. L-arginine | 19.92 | 6.86 x 10 ⁶ | -51.31 | 14.79 | 30.33 | 20.24 |
| KDP + 0.3% wt. L-lysine | 19.58 | 3.52 x 10 ⁶ | -57.74 | 14.55 | 32.044 | 20.05 |
| KDP + 0.4% wt. L-lysine | 19.47 | 4.56 x 10 ⁶ | -57.54 | 14.44 | 31.87 | 19.94 |
| KDP + 0.5% wt. L-lysine | 19.42 | 5.16 x 10 ⁶ | -57.20 | 14.39 | 31.72 | 19.89 |
| KDP + 0.3% wt. L-alanine | 19.21 | 1.45 x 10 ⁶ | -61.58 | 14.21 | 32.86 | 19.75 |
| KDP + 0.4% wt. L-alanine | 19.13 | 2.59 x 10 ⁶ | -61.21 | 14.10 | 32.64 | 19.63 |
| KDP + 0.5% wt. L-alanine | 19.07 | 3.22 x 10 ⁶ | -60.89 | 14.04 | 32.48 | 19.57 |

From table (1), one can observe that the activation energy is highest for pure KDP crystals compared to amino acids doped KDP crystals. Further, the activation energy slowly decreases from L-arginine to L-lysine and then to L-alanine. The lower values of activation energy for amino acids doped KDP crystals compared to pure KDP crystals indicates higher reaction rate for doped crystal. The doping of amino acid is expected to increase the reactivity at line defects by facilitating preferential chemical reaction. Also for a particular dopant, the activation energy decreases if the concentration of that dopant increases; contrary to this the pre-exponential factor increases. But the pre-exponential factor is higher for pure KDP crystals, compared to the doped crystals. In doped crystals the pre-exponential factor is found higher for L-arginine doped KDP crystals and then it drops for L-lysine and it has the minimum values for L-alanine doped crystals.

It has been observed by Joshi and Shah [15] that the shape of molecule plays important roles in reactivity at line defects. They have studied the effect of n-propyl alcohol and iso-propyl alcohol containing etchants on (111) cleavages of bismuth and found that the branched iso-propyl alcohol containing etchant exhibits lower reaction rate and the higher values of activation energy compared to n-propyl alcohol. The branched nature of iso-propyl alcohol produces more steric hinderance and less reactivity.

**Fig. 8 Molecular structure of L-arginine, L-lysine and L-alanine.**

The molecular structure of L-arginine, L-lysine and L-alanine is shown in figure (8). The L-arginine structure is the longest almost the three amino acids studied with two side groups, however, the complexity decreases to L-lysine and further to L-alanine. The nature of activations energy also follows the same trend. They have linear structure having hydrophobic nature and uncharged or non-ionic polar side chains. These structures are seemed to be important for reactivity at line defects in terms of motion of ledges of etch pits, in other words, the reactivity of line defects is structure sensitive of dopants used.

The pre-exponential factor value was highest for pure KDP crystal, whereas, the lower values for amino acids doped KDP crystals were observed. The pre exponential factor dropped in its value from $\approx 10^7$ for pure KDP crystals to amino acids doped KDP crystals to $\approx 10^6$, without much affecting the activation energy. The pre-exponential factor is dependent on the collision frequency and the steric factor. Therefore, it can be conjectured that the dopant amino acids reduce the steric hindrance giving rise to increased reactions sites for the attacking etchant might be due to increased steric factor and the non coplanar NH_2 in various amino acid structure. Further the pre-exponential factor also decreased in successive manner for L-arginine, L-lysine and L-alanine doped KDP crystals, respectively. The molecular structure of amino acid played important role.

3.3 Thermodynamic Parameters:

The thermodynamic parameters can be estimated for the motions of ledges of etch pits. Various thermodynamic parameters are obtained from the following standard relations [16]. The standard enthalpy of activation ($\Delta^\#H^\circ$) was calculated by using the following relation,

$$\Delta^\#H^\circ = E - 2RT \quad (2)$$

The standard change in entropy of activation ($\Delta^\#S^\circ$) could be calculated by using the following formula,

$$W = \frac{kT}{h} \cdot \exp\left(\frac{\Delta^\#S^\circ}{R}\right) \cdot \exp\left(\frac{\Delta^\#H^\circ}{RT}\right) \quad (3)$$

Where, W = Average width of etch pit, k = Boltzmann constant, h = Planck's constant, T = Absolute temperature, R = Gas constant

The standard change in Gibbs free energy of activation ($\Delta^\#G^\circ$) is possible to estimate from the following equation,

$$\Delta^\#G^\circ = \Delta^\#H^\circ - T\Delta^\#S^\circ \quad (4)$$

The standard change in the internal energy in passing from the initial to the activated state ($\Delta^\#U^\circ$) can be represented as,

$$E = RT + \Delta^\#U^\circ \quad (5)$$

Enthalpy is a state function whose absolute value cannot be known easily; it can be ascertained, either by direct method or indirectly. An increase in the enthalpy of a system, for which $\Delta^\#H^\circ$ is positive, is referred to as an endothermic process. Conversely, loss of heat from a system, for which $\Delta^\#H^\circ$ has negative value, is referred to as an exothermic process.

Entropy is a thermodynamic property of a system. It is a state function and it is defined in terms of entropy change rather than its absolute value. A spontaneous process has a natural tendency to occur, without the need for input work into the system. In contrast to this, the non-spontaneous process does not have a natural tendency to occur.

The estimated thermodynamic parameters are given in table 1. The values of the standard change in Gibbs energy of activation reduces slowly as doping concentration increases for particular doping of amino acid in KDP. Any effect, for example, that leads to a stronger binding between a solute molecule and solvent molecules will lower the enthalpy; it will lower entropy by restricting the freedom of vibration and rotation of the solvent molecules. This has been observed for amino acid doped crystals, where the values of standard change in enthalpy and entropy are lower compared to pure KDP crystals. However, change of substituent and solvent often exert their influence on $\Delta^\#H^\circ$ in a rather complex manner, but the partial compensation between $\Delta^\#H^\circ$ and $T\Delta^\#S^\circ$ is of such a nature that their influence on $\Delta^\#G^\circ$, is much simpler [17]. In the present study the negative values of $\Delta^\#S^\circ$ and moderate values of frequency factor A indicate the formation of the intermediate complex compound in etching, which has been observed earlier [18] and also may be the rate determining.

4. Conclusions:

Glacial acetic acid as an etchant revealed rhombic dislocation etch pits on the (100) surfaces of pure KDP crystals as well as selected amino acids (L-arginine, L-lysine and L-alanine) doped KDP crystals. The shape of the etch pits did not vary upon the change of temperature. The activation energy was highest for the pure KDP crystals, while its value slightly decreased in the successive manner with the doping of L-arginine, L-lysine and L-alanine, respectively. This suggested that the most stable nature of KDP crystals and on doping of amino acids it enhanced the reactivity at line defects by facilitating the extra sites for chemical reaction. The chemical structure of amino acids also played an important role. There was a systematic downward trend for standard change in enthalpy and the standard change in entropy from pure KDP and selected amino acids doped KDP crystals. Therefore, it can be inferred that the influence of amino acid doping was such that the value of $T\Delta^{\#}S^{\circ}$ and $\Delta^{\#}H^{\circ}$ compensated each other so that changes in $\Delta^{\#}G^{\circ}$ are very less for the particular amino acid doping in KDP crystals.

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